THE EFFECTS OF Cu AND Mn CONTENT AND PROCESSING ON PRECIPITATION HARDENING BEHAVIOR IN Al-Mg-Si-Cu ALLOY 6022

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Abstract

In this paper we report on an investigation of the effects of Cu and Mn content on the aging kinetics of aluminum alloys based on the 6022 composition. We varied the Cu content from 0.07 to 0.91 weight percentage and the Mn content from 0.07 to 0.60 weight percentage. This study was initiated in order to evaluate the effects of these alloy additions on alloys with application to automotive body parts. Therefore we used the paint bake temperature of current practice (177°C) as the artificial aging temperature. We were particularly interested in the effect of these additions to the early stages of the hardening process, i.e. times of 20 minutes or less. The effect of Mn was minimal on the kinetics of aging. However, Cu had a very large effect on the as quenched hardness (lower) and the kinetics of artificial aging for times less than 20 minutes. We also studied alloys that had significant amount of natural aging. In this case the Cu had a less dramatic effect of increasing the kinetics of artificial aging.
INTRODUCTION

Although the current emphasis in auto-body aluminum sheet alloy development is to improve the formability at the existing level of strength, strengthening cannot be ignored completely. The ongoing push for decreasing paint bake times and temperatures continues to impact strength levels in these products, which already tend to be underaged. Higher strengths are also always desirable for downgauge.

To maximize strengthening, any of at least three approaches might be taken:
(1) minimize the detrimental effect that natural aging (which invariably will occur in production) often has on the artificially aged strength levels
(2) improve the overall age hardenability of the alloys
(3) increase the artificial age hardening kinetics
Any of these approaches might be attacked by compositional changes or by changes in aging practices.

Unfortunately, the fundamental understanding of the impact of aging practices, changes in major alloying addition constitution and trace element additions on the mechanical properties attainable in the Al-Cu-Mg and Al-Cu-Mg-Si alloys is incomplete, despite a wealth of data. Rarely are there unambiguous comparisons. Often, if the artificial aging practices are the same, the natural aging interval, the amount of excess Si, the amount of predicted Mg$_2$Si, the amount of Cu (or other elements), or stretch level are different. Sometimes two-step aging practices or quench aging practices have been used. As a result, it is often difficult to explain observations or to predict behavior for untried compositions or practices.

The objective of this study was to obtain greater understanding of the factors affecting hardening behavior in Al-Mg-Si-Cu alloys. Alloy 6022 was chosen as a baseline and additional compositions were selected such that effects of Cu level and Mn level could be examined. In addition, the effects of the natural aging interval and the level of stretch prior to artificial aging were also studied.

BACKGROUND

(a) The Alloys

The precipitation sequence in the Al-Mg-Si alloys is generally accepted [1-3] to be:

\[ \alpha \text{(ss)} \rightarrow \beta'' \rightarrow \beta' \rightarrow \beta \]

where \( \alpha \text{(ss)} \) is the supersaturated solid solution. The \( \beta'' \) are needle-shaped zones along \(<100>\), typically 1 to 2 nm diameter and about 10 nm long. The \( \beta' \) are rod-shaped precipitates (circular cross sections) along \(<100>\), having a hexagonal crystal structure with \( a = 0.705 \text{ nm} \) and \( c = 0.405 \text{ nm} \) [2]. The \( \beta \) are platelets on \{100\} of Al having the fcc \( \text{CaF}_2 \) structure with \( a = 0.639 \text{ nm} \). It is important to note that the \( \beta \) phase seems to nucleate independently, that is the \( \beta' \) phase does not directly transform into the \( \beta \) phase. There has been some discussion of other zones, i.e. spherical ones, as precursors to the needle-shaped \( \beta'' \) zones [3].
In alloys with Cu, one should expect some Q phase, which is an equilibrium quaternary phase. The equilibrium Q phase has been indexed as having a hexagonal lattice, with the space group P6₃ [5] and lattice parameters a = 1.04 nm and c = 0.405 nm. It has 21 atoms per unit cell and hence has the Pearson symbol hP21. When it forms from the liquid, it has an irregular shape and may get as large as micron size.

When the Q phase forms during the artificial aging process we will call it Q'. In analogy with the γ' designation of Ni based superalloys this emphasizes that Q' is the same phase as Q, but has specific orientation relationships with the matrix because it forms semi-coherently. In 1984, Dumult et al. [4] called this precursor B' and others have called it L, M or Q. When it forms by solid state precipitation, it looks very similar in morphology to the β' phase in that it has a long dimension like a rod. This is the c direction of the hexagonal structure and it runs parallel to the matrix <100> directions. Since the c direction has a very similar repeat distance as the <100> of aluminum it tends to grow in these directions to minimize strain energy. In cross section the Q' precipitates have rectangular shapes with their broad faces along the {051} planes of the aluminum matrix. These habit planes are explainable, considering the lattice parameters of the aluminum and Q phase. The repeat distance along the <150> directions of the aluminum matrix is 0.404 * √26/2 = 1.03 nm. This is nearly the same as the a lattice parameter of the Q phase. Hence during the solid state precipitation Q' minimizes its surface energy by maximizing its area on the {051} planes. Thus, overall, the Q' phase is lath shaped.

There are a large number of commercially significant Al-Mg-Si-Cu alloys. While 6061 is one of the oldest alloys, alloy 6063 is quite common for use in automotive extrusions and alloys 6009, 6111 and 6016 have been produced as sheet for automotive applications. More recently, alloy 6022 had been developed for sheet applications as well [6]. It is relatively high solute alloy with Si in excess of that needed to form the equilibrium Mg₃Si, β phase. 6022 contains 0.08% Mn (throughout the paper we give composition in weight percentage) for grain structure control and 0.08% Cu for strength. Fe levels are minimized for the best formability.

(b) Processing Considerations

The Al-Mg-Si-Cu alloys require processing typical for heat treatable aluminum alloys, i.e. homogenization, fabrication, solution heat treatment, quenching and artificial aging. In the case of autobody sheet alloys, the sheet is typically provided in the T4 temper (i.e. after solution heat treating and quenching), formed and then subjected to a complex paint bake process where the artificial aging occurs. As a result, alloy/product developers have little ability to control the natural aging interval between quenching and artificial aging (i.e. paint baking) nor can they control the artificial aging practice. Therefore, it is important to develop alloys/products whose properties are relatively insensitive to these processing variables. Ideally, one would produce an alloy with rapid hardening kinetics and slow overaging kinetics such that even the shortest paint bake practice would produce a strong material.

Unfortunately, the properties of the Al-Mg-Si-Cu alloys tend to be sensitive to many processing variables, but the one which has received the greatest attention is the natural aging interval. Some Al-Mg-Si alloys (like 6061 without Cu additions, [7]) exhibit a deleterious effect of natural aging on subsequent artificial aging, others exhibit a beneficial effect (as in 6060, [8]) and still others show no effect. Presumably, this is due to the decomposition which occurs at room temperature, a process whose rate must depend on solute supersaturation, number of excess vacancies, presence of certain trace elements, and other things. This topic has been addressed very

EXPERIMENTAL DETAILS

(a) Alloy Fabrication

Five Al-Mg-Si-Cu alloys were cast as 50 mm x 250 mm x 360 mm ingots. The actual compositions are given in Table I. The compositions were chosen such that the effects of Cu and Mn in 6022 could be examined separately. Alloy 485 is the 6022 control, alloys 494 and 498 are medium and high Cu variants and alloys 502 and 503 are medium and high Mn variants.

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>Composition, wt.%</th>
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<tbody>
<tr>
<td></td>
<td>Mg</td>
<td>Si</td>
</tr>
<tr>
<td>485</td>
<td>0.58</td>
<td>1.28</td>
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<tr>
<td>494</td>
<td>0.56</td>
<td>1.24</td>
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<tr>
<td>498</td>
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<tr>
<td>502</td>
<td>0.54</td>
<td>1.33</td>
</tr>
<tr>
<td>503</td>
<td>0.54</td>
<td>1.36</td>
</tr>
</tbody>
</table>

The ingots from alloys 485, 502 and 503 were homogenized for 6 h at 571°C and the ingots from alloys 494 and 498 were homogenized for 4h at 560°C after using a stepped practice to get from 504°C to 560°C. All of the ingots were reheated to 482°C, soaked for 0.5 h and hot rolled in 5 passes to 6.3 mm. Hot rolled pieces were then annealed for 1 h at 560°C and cold rolled in 4 passes to 1.9 mm thick sheet.

(b) Heat Treatment and Aging

All sheet samples were solution heat treated for 20 minutes at 571°C and cold water quenched. One set of samples from each composition was not stretched. Another set of samples from several compositions, i.e. 485, 502 and 503 was given a 2% stretch prior to artificial aging.

All samples were artificially aged for times of 0, 5, 20, 50, 200, 500 and 1000 minutes at 177°C. In order to obtain rapid and consistent heat up rates to the artificial aging temperature, all specimens were heated initially in a lead bath. Those samples which were to be aged 50 minutes or less were aged entirely in the lead bath. Samples which were to be aged for the longer times were heated up in the lead bath, and then, once the aging temperature was reached, they were transferred to an air furnace to complete the aging. All specimens were quenched to room temperature at the completion of aging.

In one set of samples, the natural aging interval between quenching and artificial aging (or between stretching and artificial aging) was limited to a few minutes or less. In another set of samples from selected compositions, a natural aging interval of either 9 or 30 days was applied prior to artificial aging.
(c) Characterization

Three Rockwell 15T Hardness measurements were taken and averaged for all samples. Transmission electron microscopy (TEM) and differential scanning calorimetry (DSC) were performed on selected samples from alloys 485 and 498 to explain the hardness data.

RESULTS

(a) Effect of Cu

The Cu level has a large effect on the hardening kinetics and a smaller but noticeable effect on the maximum hardness which can be achieved in 6022-type alloys. Figure 1 presents hardness as a function of artificial aging time for alloy 485 (6022 control) and alloys 494 and 498 (the medium and high Cu variants, respectively). Here, none of the 6022 variants were naturally aged prior to artificial aging. Increases in Cu increased the kinetics of precipitation substantially and increased the peak hardness modestly, yet had little effect on the time to peak hardness. The hardnesses of the medium and high Cu variants were substantially greater than that of the 6022 control, especially in the range from 20 to 50 minutes of artificial aging at 177°C, which is significant since paint bake practices are expected to fall in this range. Surprisingly, increasing the Cu from the level of 0.07% in alloy 485 (6022 control) to a level of 0.3% in alloy 494 had very little impact on the initial hardness. Further increases to the level of 0.9% in alloy 498 led to a significant decrease in the initial hardness.

The effect of Cu is somewhat diminished in naturally aged samples as compared to those which were not naturally aged. Figure 2 presents hardness as a function of artificial aging time for samples of alloy 485 (6022 control) and alloy 498 (the high Cu variant) which had been naturally aged 30 day between quenching and artificial aging. Both hardness traces show the expected initial decrease which can be attributed to reversion of the zones which had formed during natural aging. While increases in Cu level still produced increases in the kinetics of precipitation, there was essentially no impact on the peak hardnesses and there was a smaller increase in the hardnesses in the range from 20 to 50 minutes of artificial aging than was observed in the samples which had not been naturally aged.

DSC curves for alloys 485 and 498, taken at a heating rate of 10°C/min, are displayed in Figure 3. The first exothermic peak on the curves, centered at around 90°C, is considered to be due to the formation of G.P. zones. For alloys naturally aged for 30 days, no exothermic peaks around 90°C were observed on the DSC curves, suggesting that the zones corresponding to the peak already formed during natural aging. The second peak, at 245°C, is important for precipitation hardening and is usually designated as the formation of β". To reveal the precipitates corresponding to this peak, alloys 485 and 498 were heated in the DSC to a temperature just above the second peak. The TEM micrographs for these samples are shown in Figures 4 and 5, respectively. The precipitates presented in the micrographs are typical β". It can also be seen that the microstructure of the high Cu alloy is much finer than that of the lower Cu alloy. This helps to explain the higher hardness of the high Cu alloy after 20 minutes of artificial aging at 177°C. The TEM images of peak aged samples are more similar to each other. The higher Cu alloy shows evidence of Q' precipitation [12].
FIGURE 1. Dependence of hardness on artificial aging time at 177°C for alloys with different Cu levels.

FIGURE 2. Hardness as a function of artificial aging time at 177°C for alloys 485 (0.07% Cu) and 498 (0.91% Cu) after naturally aged for 30 days.
FIGURE 3. DSC curves for alloys 485 (0.07% Cu) and 498 (0.91% Cu).

(b) Effect of Mn

The Mn level had very little effect on the peak hardnesses which developed in the 6022 variants, regardless of whether they had or had not been naturally aged prior to artificial aging. Figure 6 presents hardness as a function of artificial aging time for alloy 485 (6022 control), alloy 502 (medium Mn variant) and alloy 503 (high Mn variant) samples which had not been naturally aged. Although increases in Mn level led to increases in initial hardness, presumably due to solid solution hardening, the changes in the peak hardness and the hardening kinetics were small. Figure 7 presents the same information for samples which had been naturally aged for 9 days. Mn level did appear to affect hardness values in the underaged regime.

(c) Effect of Natural Aging Interval

Natural aging appeared to have a slight beneficial effect on the peak hardnesses which developed in alloy 485 (6022 control) but essentially no effect on the peak hardnesses which developed in alloy 498 (high Cu variant). Figure 8 presents hardness as a function of artificial aging time for alloys 485 and 498 which were given either no natural aging or 30 days of natural aging between quenching and artificial aging. Naturally aged samples of the control and the high Cu variant had the expected higher initial hardnesses when compared to samples which had not been naturally aged. The naturally aged samples showed decreases in hardness upon initial artificial aging which may be attributed to reversion of the zones formed during natural aging. Hardness then began to increase to similar or higher peak hardnesses than the counterparts which had not been naturally aged. The times required to reach peak hardness were slightly affected, if at all.
FIGURE 4. TEM micrographs of alloy 485 (0.07% Cu) corresponding to the second DSC peak. (a) Bright-field image; (b) Dark-field image.
FIGURE 5. Microstructure of alloy 498 (0.91% Cu) corresponding to the second DSC peak. (a) Bright-field image; (b) Dark-field image.
FIGURE 6. Variation of hardness with artificial aging time at 177°C for alloys 485 (0.08% Mn), 502 (0.30% Mn) and 503 (0.60% Mn).

FIGURE 7. Dependence of hardness on artificial aging time at 177°C for alloys 485 (0.08% Mn), 502 (0.30% Mn) and 503 (0.60% Mn) after naturally aged for 9 days.
FIGURE 8. Hardness as a function of artificial aging time at 177°C for alloys 485 (0.07% Cu) and 498 (0.91% Cu) with and without natural aging (NA).

FIGURE 9. Variation of hardness with artificial aging time at 177°C for alloys 502 (0.30% Mn) and 503 (0.60% Mn) with and without natural aging (NA).
The effects of natural aging were significant in samples which were artificially aged to the underaged conditions, with the effect being larger in the high Cu variant than in the 6022 control. For artificial aging times of 20 to 50 minutes, the samples which were not naturally aged reached substantially higher hardnesses than the samples which had been naturally aged for 30 days.

Mn levels appeared to have an effect on how the 6022 variants were affected by the natural aging interval. Figure 9 presents hardness as a function of artificial aging time for alloy 502 (medium Mn variant) and alloy 503 (high Mn variant). The 6022 variants with the higher levels of Mn obtained somewhat higher peak hardness in samples which had been naturally aged compared with those which had not. Also, the naturally aged samples showed the expected decrease in hardness upon initial artificial aging due to reversion. It is interesting to note that the high Mn levels appeared to stabilize the naturally aged alloy somewhat. Both alloys 502 and 503 showed lower drops in hardness upon reversion than alloy 485 with its standard Mn level (refer back to Figure 8 for data on alloy 485). This becomes especially important if artificial aging times of 20 or 50 minutes are considered, since for these times the high Mn alloy, regardless of whether it was naturally aged or not, develops much higher hardness than the 6022 control.

(d) Effect of Stretch Level

The application of a 2% stretch prior to artificial aging increases hardness throughout most of the artificial aging process although the effect is diminished as peak hardness is reached. Figure 10 presents hardness as a function of artificial aging time for samples of alloy 485 (6022 control) which had not been stretched and samples which were stretched 2%. Included are data for the samples which had not been naturally aged and for those which had been naturally aged for 30 days. The beneficial effect of stretching was the most significant for samples artificially aged for 20 minutes, since the precipitation hardening appears to overcome the reversion process more rapidly in stretched samples than in the unstretched samples.

The effects of a 2% stretch in alloy 498 (high Cu variant) and in alloy 503 (high Mn variant) are similar to that described for the 6022 control although the former may be smaller in magnitude. Figures 11 and 12 illustrate this in the plots of hardness versus artificial aging time for alloys 498 and 503, respectively.

DISCUSSION

There have been a number of previous studies which have tried to clarify the role of Cu and the role of natural aging interval and the interaction between the two in Al-Mg-Si-(Cu) alloys [13 - 19]. Fewer studies are available on the effects of dispersoid forming elements. Many indicate that Cu enhances the age hardening and lessens the deleterious effects of natural aging but there are some subtle differences between observations made in the different studies.

Many of the studies had focused on alloys whose Mg and Si contents were balanced to produce Mg2Si. In such alloys, Pashley, Rhodes and Senderek [13] found that strengthening was suppressed during natural aging in the Cu-containing alloys, thereby delaying the deleterious effect of natural aging on the artificially aged strengths. The presence of Cu led to a much finer precipitate structure in the artificially aged samples and the beneficial effect of Cu was greater if
FIGURE 10. Effects of natural aging and 2% stretch on the hardness for alloy 485 (0.07% Cu) artificially aged at 177°C for different times.

FIGURE 11. Effect of 2% stretch on the hardness for alloy 498 (0.91% Cu) artificially aged at 177°C for different times.
higher artificial aging temperatures were used. Tamizifar and Lorimer [14] and Chatterjee and Entwistle [15] also found that Cu increased the final artificially aged hardness and that it delayed the deleterious effects of natural aging. The results of Chatterjee and Entwistle and Livak [16] supported the Pashley et al. observation that the reason for the enhanced strength in the Cu-containing alloys was a much finer distribution of precipitate. Tamizifar and Lorimer [14] reported that Cu did not affect the artificial aging time required to reach peak hardness.

Yokota et al. [17] looked at varying Cu levels in alloys whose Mg and Si contents were balanced to produce Mg$_2$Si as well as in alloys with excess Si and in alloys with excess Mg. The Cu additions did not suppress hardening during natural aging for any of their alloys. In all instances, the Cu additions did enhance the age hardening strength levels through the entire artificial aging process. Suzuki et al. [18] also studied balanced alloys and alloys with excess Si and excess Mg. They found that higher Cu levels always led to higher artificially aged strengths and suppressed overaging. The maximum hardness was always lower in samples which had been naturally aged prior to artificial aging, but the degree of lowering decreased with increasing Cu content despite the fact that increasing Cu contents led to increasing clustering during natural aging. When Cu was added to the alloys with excess Si, no Q or Q' formation peaks were observed in differential scanning calorimetry traces.

The current study, which deals with an excess Si alloy, is not consistent with most others in that relatively large Cu additions had no effect at all or quite a small effect on the peak hardnesses which developed during aging at 177°C. Recall, that when there was no natural aging, there was a modest improvement in hardness associated with Cu additions (Figure 1). When 30 days of natural aging had been applied, there was no benefit in peak hardness associated with the Cu additions (Figure 2). This observation is most consistent with the study of Sakurai and Eto [19] who also looked at Cu effects in an alloy with excess Si. They found that Cu enhanced the aging
kinetics and peak strengths if artificial aging was carried out at 200°C but not at 150°C or 170°C. They reported that Cu additions produced finer and more numerous β' and that some θ' was also present but the latter was not associated with strengthening. Also, it may be that the differences are related to the precipitation of the Q' phase in the higher Cu alloy [12]. The current study is consistent with others in that the Cu additions clearly enhanced artificial aging kinetics, especially in the underaged regime. This is very important since typical paint bake practices will produce an underaged condition.

The effect of Mn is this study was very small. One might have expected such an addition to affect the clustering which occurs during natural aging either through an interaction between vacancies and Mn solute or through Mn-bearing dispersoids serving as vacancy sinks. Mn did appear to stabilize the naturally aged microstructure since the naturally aged alloys with 0.3% Mn and 0.6% Mn finished reversion and began to harden more quickly than the alloy with 0.08% Mn although a direct comparison is not available. (The alloy with 0.08% Mn had been naturally aged for 30 days while the other alloys had been aged for only 9 days. Hence, data from the former was not included in Figure 9.)

Processing techniques such as step quenching, pre-aging and reversion aging are being studied in an effort to enhance the artificial aging kinetics at the 177°C [20].

**CONCLUSIONS**

1. The Cu level has a large effect on the hardening kinetics and a smaller effect on the maximum hardness which can be achieved in 6022-type alloys, although its effect is somewhat diminished in naturally aged samples as compared to those which were not naturally aged.

2. The Cu causes a refinement in the microstructure. We believe that Cu promotes the kinetics of artificial aging due to the formation of the Q' phase in addition to the phases which precipitate in lower Cu alloys.

3. The Mn level had very little effect on the peak hardesses which developed in the 6022 variants, regardless of whether they had or had not been naturally aged prior to artificial aging. However, high levels of Mn did appear to provide a beneficial effect on the hardness of the underaged condition.

4. Natural aging appeared to have a slight beneficial effect on the peak hardesses which developed in the 6022 control and the high Mn variant but essentially no effect on the peak hardesses which developed in the high Cu variant. Unfortunately, natural aging had a noticeable deleterious effect on the hardesses of the underaged condition in the 6022 control, the high Cu variant and the high Mn variant.

5. The application of a 2% stretch prior to artificial aging increases hardness throughout most of the artificial aging process although the effect is diminished as peak hardness is reached. The beneficial effect of the stretch is most significant for aging times around 20 minutes.
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