Rapid Age-Hardening Behavior of Al–Mg–Cu (–Ag) Alloys and Incubation Stage in the Low-Temperature Aging

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The characteristic age-hardening response of Al–3.0Mg–1.0Cu (mass%) alloys with and without Ag addition has been investigated by the hardness measurement, differential scanning calorimetry (DSC) and electrical resistivity measurement. The alloy compositions locating in the (α+S+T) phase field of the Al–Mg–Cu phase diagram are known to be effective to harden in two stages separated by a distinct and often prolonged hardness plateau. The first stage of hardening occurs very rapidly (e.g., within 60 s at 443 K) and contributes to increase hardness as much as 50% of the total age-hardening. After the first stage of hardening, a clear plateau stage is observed in the hardness curve. In the low temperature aging, the characteristic incubation stage at which no clear hardness increase and electrical resistivity increase appears for a long time before the first stage of hardening. The origin of the both incubation and plateau stages is discussed based on the nanocluster formation and vacancies. The influence of the Ag addition on the precipitation behavior is also discussed in terms of the atom-atom interaction.

Keywords: aluminum–copper–magnesium alloy, rapid age-hardening, incubation stage, plateau stage, nanoclusters

1. Introduction

Al–Mg alloys have been utilized as a light-weight body sheet material for automobiles due to their well-balanced properties of mechanical strength, ductility and press-formability. Although these alloys are non-heat treatable, their strength can be increased by the addition of copper because Al–Mg–Cu alloys give rise to the precipitation strengthening phenomena.1) Aside from the more numerous studies of Al–Cu–Mg alloys, some attention has also been paid to the Al–Mg–Cu alloys (closely related to 5000 series aluminum alloys). The strengthening of Al–Mg–Cu alloys is based on a precipitation hardening through the sequence as follows:

\[
\alpha(\text{SSSS}) \rightarrow \text{Cu/Mg nanoclusters} \rightarrow \text{GPB zones} (S') \rightarrow S' \rightarrow S(\text{Al}_2\text{CuMg})
\]

where SSSS is the super saturated solid solution. Cu/Mg clusters are considered as precursors of the Guinier-Preston-Bagaryatsky (GPB) zones. One characteristic of their aging behavior is that hardening occurs in two distinct stages separated by a plateau, where the hardness may remain constant for a long time. The behavior of the Al–Mg–Cu alloy is similar to that of the Al–Cu–Mg alloys. The first stage, which occurs very rapidly (e.g., within 60 s at 443 K) and may contribute as much as 60% of the total hardening, is now attributed to solute clustering rather than to the formation of GPB zones. This rapid hardening phenomenon (RHP) has been termed as “cluster hardening”. GPB zones or the S’ phase were not detected until later in the aging process and they are considered to be the source of the second stage of hardening. Although some researchers propose the dislocation-solute atom interaction as the origin of RHP, there is still no unified interpretation.

The small addition of some alloying elements has been recognized to be effective to control precipitate micro-

structures and alloy properties.2–5) According to the previous work,6) the small addition of Ag is extremely effective to improve age-hardening response of the Al–Mg–Cu alloy. By adding Ag, dense and homogeneous distribution of fine particles can be obtained and age-hardening is greatly enhanced. The micro beam electron diffraction (MBED) study by Chopra et al.7) indicates that the fine precipitates in the Al–1.5Cu–4.0Mg–0.5Ag (mass%) alloy, which lies in the (α+S+T) phase field, are not isomorphous with the T phase. They proposed that the microstructure of this alloy is dominated by the Z phase. Omura et al.8) observed several phases in the Al–3.0Mg–1.0Cu–0.4Ag alloy. They also found that the Z phase is formed in the Al–3.0Mg–1.0Cu ternary alloy.

The aim of this study is to investigate the origin of the rapid hardening behavior of the Al–Mg–Cu alloy and the effects of small addition of Ag on the age-hardening behavior and microstructures.

2. Experimental Procedure

The chemical compositions of the alloys utilized in this work are listed in Table 1. The specimens were solution treated in a salt bath at 793 K and kept for 60 s, followed by iced-water quenching for 60 s. These specimens are called as the as-quenched (A.Q.) alloys in this paper. An aging treatment was carried out in an oil bath at 323–443 K for various times. Micro-Vickers hardness was measured with a load of 500 g for 15 s using Mitsutoyo HM-102. Differential scanning calorimetry (DSC) was carried out using a Rigaku equipment of DSC8230 with 40 mg of pure Al (99.99%) as a reference under an argon atmosphere with heating rate of 10 K/min.

Table 1 Chemical compositions of the alloys (mass%).

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Cu</th>
<th>Ag</th>
<th>Al</th>
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<tbody>
<tr>
<td>Base</td>
<td>3.04</td>
<td>0.97</td>
<td>—</td>
<td>Bal.</td>
</tr>
<tr>
<td>Ag-added</td>
<td>3.07</td>
<td>0.98</td>
<td>0.41</td>
<td>Bal.</td>
</tr>
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0.167 K/s. The range of temperature for the DSC measurement was set from 223 to 773 K using a liquid nitrogen controller. Electrical resistivity measurements were also performed by a four-probe method with the specimens prepared as wires with the diameter of 1.0 mm and the gage length of 300 mm.

3. Results

3.1 Hardness changes

Figure 1 shows the composition location of the Base alloy. The Base alloy is located at (α+S+T) phase field as shown in Fig. 1. The chemical compositions of the Base and Ag-added alloys are shown in Table 1. The results of micro-Vickers hardness changes during aging at various temperatures are shown in Fig. 2. In both alloys, marked increase of hardness occurs in the initial stage, the first stage of hardening, and then, the hardness remains almost constant for a long time, the plateau stage, finally, the hardness reaches at the peak, the second stage of hardening. In the Ag-added alloy, the hardness change during the first stage of hardening is larger and the plateau stage is shortened as a result of the fast arrival of the second stage of hardness. Small amount of Ag changes the age hardening response of the Base alloy dramatically. According to the change of aging temperature, the hardening response is delayed. Only one-step of hardening is observed at temperatures below 353 K while three-step of hardening is observed above 353 K. The starting time, t, of the first stage can be well described by a linear relation with the inverse Temperature, 1/T, the Arrhenius plots (Fig. 3(a)). The activation energy of the Base alloy is 141 kJ/mol. The one of the Ag-added alloy is 122 kJ/mol. It indicates that the Ag-addition can lower the activation energy of the first stage response. Figure 3(b) shows the hardness at the plateau stage. In the Base alloy, the lower aging temperature leads to a little higher hardness. On the contrary, in the Ag-added alloy, the lower aging temperature leads to a little lower hardness.
3.2 Differential scanning calorimetry (DSC)

DSC is a useful technique to detect very small nanoclusters and analyze precipitation sequences. DSC results of A.Q. specimens of the (a) Base alloy and (c) Ag-added alloy are shown in Fig. 4. In both alloys, there is a large exothermic peak A at around 370–420 K. At around 540–650 K and 600–650 K, there are peaks C and D. The peak A is attributed to the formation of nanoclusters of solute atoms. According to the previous report,9) the peak D is attributed to the precipitation of the S* phase which is the strengthening phase in the Base alloy. The peak C is observed notably in the Ag-added alloy. It is attributed to the precipitation of the Z phase which is fine and almost spherical and greatly contributes to strengthen the Ag-added alloy. After aging for 1.2 ks at 443 K, the plateau stage of hardening, the peak A disappeared in both alloys. It suggests that nanoclusters cause the first stage of hardening. An endothermic peak B is observed only in the Base alloy. It is attributed to the dissolution of the pre-formed nanoclusters. The Ag addition can improve the thermal stability of nanoclusters.

Figure 5(a) shows age-hardening curves of the Base and Ag-added alloys aged at 443 K. At various aging times \((t_1)\)–\((t_5)\), the DSC analysis is performed (Figs. 5(b) and 5(c)). In the case of aging times before the second stage of hardening \((t_1)\)–\((t_3)\) in the Base alloy and \((t_1)\)–\((t_2)\) in the Ag-added alloy, there is no change in the peaks C and D. It suggests that there are no precipitates such as the S* or Z phase and nanoclusters are dominant. On the other hand, long aging times at which hardness is near the peak, \((t_4)\)–\((t_5)\) in the Base alloy and \((t_1)\)–\((t_3)\) in the Ag-added alloy, lead to the change of the peaks C and D. Both peaks gradually disappear. It indicates that the S* or Z phase precipitates are formed in this stage. The plateau stage is the incubation for the precipitation of the S* or Z phase and aggregation of the nanoclusters formed at the first stage of hardening.

Figure 6(a) shows the age-hardening curves of the Base and Ag-added alloys aged at 323 K. At various aging times \((t_1)\)–\((t_5)\), the DSC analysis is performed (Figs. 5(b) and 5(c)). In the case of aging times before the first stage of hardening \((t_1)\)–\((t_4)\), there are peaks A, C and D in both alloys. It suggests that nanoclusters are not formed yet during the first stage of hardening. On the other hand, after the hardness increase rapidly \((t_5)\), the peak A disappeared, suggesting that the formation of nanoclusters is completed. Accordingly, nanoclusters are formed in the first stage of hardening and the stage at which no clear hardness increases is the incubation for the formation of nanoclusters. Low aging temperature requires a long period for the formation of nanoclusters.
3.3 Electrical resistivity changes

Figure 7 shows the electrical resistivity increment, $\Delta \rho$, during aging at 443 K in both alloys. Although various elements affect the electrical resistivity, the electrical resistivity, $\rho$, of alloys containing solute elements, GP zones or precipitates is generally described by the following equation.

$$\rho = \rho_0 + \rho_s + \rho_p$$  \hspace{1cm} (2)

$\rho_0$ is the contribution to the electrical resistibility due to the phonon scattering in aluminum. $\rho_s$ is the residual resistance of the solute atoms in the matrix. $\rho_p$ is the contribution to the electrical resistivity by precipitates. Since $\rho_0$ is originated in the lattice vibration of aluminum, it does not change during isothermal aging treatment only depending on temperature. $\rho_s$ is dependent on the solute concentration in the matrix. Since solute concentration decreases with the progress of the phase decomposition, this value decreases with aging time, and if it reaches the balanced solute concentration at the temperature, it will turn into a certain value. Although $\rho_0$ is 0 in a perfect supersaturated solid solution, it changes with formation of solute clusters and is given by the product of function of the number density $N$ and size $D$, $G(D)$.

$$\rho_p = N \cdot G(D)$$  \hspace{1cm} (3)

Since the contribution by the increase in the number density of clusters and GP zones is large in the early stage of the phase decomposition, electrical resistivity dramatically increases and then, the number density of GP zones markedly decreases resulting in the decrease in the resistivity even the average size becomes increased. Then, the electrical resistivity change generally shows a maximum by those balances.

In both alloys, after the incubation period, electrical resistibility goes up rapidly at the first stage, passing the maximum and decreases gradually at the plateau stage, and then, decreases rapidly at the second stage. The maximum is observed within 60–120 s. In the Ag-added alloy, the amount of the resistivity increment is larger than that of the Base alloy. It is suggested that the volume fraction of the nanoclusters is larger in the Ag-added alloy in the first stage. The rapid fall of the electrical resistibility in the second stage is due to the formation and growth of precipitates. Since the electrical resistivity falls greatly and more quickly in the Ag-added alloy, the formation of precipitates is promoted by the Ag addition. The plateau stage is considered to be the incubation period for the precipitation and the change of the electrical resistibility corresponds to that of hardness.

At 323 K, the incubation stage where no resistivity changes for a long time is observed as shown in Fig. 8. After the incubation stage, the electrical resistibility gradually increases and goes up rapidly at the first stage and becomes a certain value at the plateau stage. The relationship between
the hardness and electrical resistibility changes is shown in Fig. 9. There is a stage where the electrical resistibility increases gradually with almost no change in the hardness as observed in Fig. 9. According to the result of the DSC measurement, nanoclusters are not formed before the first stage. The change of the electrical resistivity suggests the existence of the process in which the solute atoms aggregate to form nanoclusters. Then, nanoclusters contribute to increase electrical resistivity and hardness rapidly.

At the plateau stage, the electrical resistivity at 323 K is larger than that at 443 K aging in the both alloys. It suggests that finer nanoclusters are formed by aging at 323 K and the microstructure might be dramatically changed.

4. Discussion

The characteristic age-hardening behavior of the Al–Mg–Cu alloy was found and is schematically illustrated in Fig. 10. Three stages of age-hardening were found; i.e., the first stage, the plateau stage and the second stage of hardening as shown in Fig. 10. In the present work, the first and second stages are attributed to the formation of nanoclusters and precipitates, respectively. The nanoclusters of solute atoms are clearly detected in the plateau stage of the Base alloy by the 3DAP method and are shown in Fig. 11.8) The nanoclusters are enriched in Mg and Cu atoms. In the later of the plateau stage or beginning of the second stage some of the elongated precipitates of the S' phase were partly observed (Fig. 11(c)). The TEM observation clearly revealed that the precipitates in the second stage are the S' and Z phases. The plateau stage is mainly due to the incubation for the formation of precipitates. The plateau stage becomes shorter when the aging temperature is higher. The formation of nanoclusters occurs rapidly in the first stage and greatly affects the hardening of the alloy. The nanoclusters of the Al–Mg–Cu alloy are found to be very effective to increase the hardness rapidly, suggesting the existence of the “cluster hardening” proposed by Ringer et al.10,11) It is also interesting that the incubation stage before the first stage is found at lower aging temperatures in the present work. This is very different from the case of Al–Cu alloys12) which show almost no incubation stage as shown in Fig. 12. Typically at lower aging temperatures the electrical resistivity increases rapidly as indicated in Fig. 12 in Al–4%Cu alloy aged at 333 K.10) The rapid increase of the electrical resistivity is designated as the fast reaction stage. The fast reaction stage appears due to the enhanced diffusion of Cu atoms by the quenched-in excess vacancies. The fast reaction stage is generally observed in the age-hardening aluminum alloys such as Al–Cu–Mg, Al–Mg–Si, Al–Zn and Al–Zn–Mg alloys. The activation energy for the fast reaction is determined as 50–80 kJ/mol in the Al–Cu alloy, lower than that of the conventional diffusion of Cu atoms in Al (≈130 kJ/mol). The estimated activation energy for the first stage hardening of the Al–Mg–Cu alloy in the present work is 141 kJ/mol, almost equal to the activation energy of the conventional diffusion of Cu. Therefore, one of the possible explanations for the initial incubation stage of the Al–Mg–Cu alloy is that the excess vacancies are preferentially trapped by Mg atoms just after quenching. The interaction between a Mg atom and vacancy is strongly attractive. Then, Mg-Vac co-clusters (Vac: vacancy) are expected to be formed in the incubation stage. The Cu composition of the present Al–Mg–Cu is very low compared with the Mg composition (Mg...
3.38 mol%, Cu: 0.40 mol% in the Base alloy). Therefore, it must be difficult to meet Mg-Vac co-clusters and Cu atoms together and it takes time to form Mg/Cu/Vac nanoclusters, resulting in the incubation stage. This is different from the Al–Cu–Mg alloys containing high Cu.

Although hardness and electrical resistivity are almost constant in the incubation stage, it is assumed that some changes of co-cluster formation occur in the alloy. The rapid increase of hardness is observed in the Al–Cu–Mg alloys containing high Cu.10,11,13–15 There are many arguments, however, about what causes the first hardening stage and no clear understanding is obtained so far. Ringer et al. proposed the “cluster hardening” caused by clustering of Cu and Mg atoms.10,11) Ratchev et al. reported that the S″ phase which nucleates heterogeneously on dislocations is responsible for the rapid hardening.13) Reich, Nagai and others also proposed that the main factor of the initial hardening is the strong interaction between solute atoms and dislocations.14,15)

Various microalloying elements have so far been tried for the age-hardening improvement of Al–Mg–Cu alloys.2–5 It is clarified that the effect of the Ag addition is the largest.6) Figure 13 shows schematic illustration of the phase transformation sequence in the (a) Base and (b) Ag-added alloys. Since Ag has the strong interaction with Mg and vacancies, Mg/Ag/Vac clusters are easily formed in the Al–Mg–Cu–Ag alloy in the early stage of age hardening. The interaction between Mg and vacancies is also strong as already described. The sequence in the initial stage is again discussed here. In the initial stage it can be assumed that the Mg/Ag/Vac clusters will be formed and then Cu atoms gradually aggregate to Mg/Ag/Vac clusters to form Mg/Cu/Ag clusters. This result is experimentally obtained by the 3DAP analysis.8) Compared with Mg/Cu clusters in the Base alloy, Mg/Cu/Ag clusters are thermally more stable as indicated by the DSC results because of the strong interactions among atoms.
The higher thermal stability is also useful to act as strong obstacles for the dislocation movement resulting in high mechanical strength in the Al–Mg–Cu–Ag alloy. As is already reported\(^5,8\) the microalloying element of Ag dramatically changes the precipitation; i.e., the Z phase is preferentially formed in the Al–Mg–Cu–Ag alloy. The morphology and structure of the Z phase is already reported in the previous paper.\(^5,8\) However, the details of the formation mechanism of the Z phase in the initial stage are not clear. The relationship between Mg/Cu/Ag nanoclusters and the Z phase will be further investigated.

It is interesting that almost no change in hardness occurs at room temperature before 2592 ks in the Base alloy and 604.8 ks in the Ag-added alloy. The artificial aging at higher temperatures leads to the rapid increase of hardness even after the prolonged exposure at room temperature. This feature is very suitable for the bake-hardening response for car body panels. At room temperature, it is easy to do press forming and then during paint baking hardness rapidly increases within several minutes at comparatively low temperatures. These properties will be much improved by controlling optimum alloy compositions and microalloying elements.

Another interesting feature of age-hardening of Al–Mg–Cu alloys is the hardness at the plateau stage for different aging temperature. The hardness at the plateau stage is almost similar even the aging temperature is different as shown in Fig. 2. In general, the age-hardening level decreases when aging temperature increases. However, the tendency is different in the present alloys. This feature is also suitable in the industrial process. The reason is not clear at the moment. This phenomenon will be also investigated further and will be reported.

5. Conclusions

Age-hardening behavior of the Al–Mg–Cu (–Ag) alloys was investigated using hardness, DSC and electrical resistivity measurements. The obtained results are summarized as follows.

(1) The Al–Mg–Cu alloy shows three stages of age-hardening reactions, the first hardening stage, plateau stage and second hardening stage. It is understood that the first, plateau and second stages are attributed to the nanocluster formation, the incubation period and the formation of precipitates, respectively.

(2) There is a characteristic stage where no hardness increase occurs before the first hardening stage. The electrical resistivity is also almost unchanged. From the DSC results, this stage is an incubation stage for the formation of nanoclusters. The existence of the incubation stage is different from the general age-hardenable aluminum alloys.

(3) The Ag addition can improve thermal stability of nanoclusters. Since the interactions among atoms are strong, Mg/Cu/Ag nanoclusters can exist at high temperatures. The high stability is also effective to act as strong obstacles for moving dislocations. In the Ag-added alloy, the precipitates are mainly the Z phase.

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REFERENCES