### EFFECT OF COPPER AND MAGNESIUM CONTENTS AND QUENCHING RATE ON AGE HARDENING BEHAVIOR OF 2000 SERIES ALUMINUM ALLOYS

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### ABSTRACT

The effect of the copper and magnesium contents and quenching rate during quenching on the age hardening behavior of 2000 series aluminum alloys was investigated. For the higher copper-containing specimens as conventional alloys, like AA2024, precipitation of the stable phases increased as the quenching rate decreased under the as-quenched conditions. The maximum hardness after the artificial aging of air cooled (AC) specimens was much lower than that of the water quenched (WQ) specimens. On the other hand, for the lower copper-containing specimens, coarse precipitation did not increase even in the case of the AC. The age hardening behaviors of the WQ and AC were very similar such that the maximum hardness and aging rate were almost the same. Many parts of the fine precipitates that increased the hardness were thought to be the GPB zone or fine S' phase for the WQ and relatively coarse S' phase for the AC. From the calculated CCT (continuous cooling transformation) diagrams, the lower copper-containing specimens could maintain the copper and magnesium in the solid solution state during the AC, so they could be quenched at a rather slower quenching rate like the AC.

## **KEYWORDS**

Al-Cu-Mg alloy, Quenching rate, Age hardening, Precipitation, CCT diagram

#### **INTRODUCTION**

The 2000 series aluminum alloys, containing copper and magnesium as the major chemical components, are some of the well-known heat treatable aluminum alloys. These alloys have a high quenching sensitivity, thus the age hardening ability of these alloys decreases with a slow quenching rate. To prevent the decrease of the age hardening ability, quenching is done by a method such as water quenching, which is not very efficient in an industrial situation, because the method requires such large equipment. For these alloys, reducing the quenching sensitivity helps them to be produced in a rather convenient way. For example, 6000 series alloys such as A6063 have low quenching sensitivity, thus they could be quenched by only air cooling just after extrusion and they do not need water quenching. Based on these reasons, investigations of these alloys with high copper and magnesium contents have been conducted in the past to find a way to lower the quenching sensitivity by adding transition elements such as manganese, chromium and zirconium (Kanno, Suzuki, & Itoh, 1986; Suzuki & Itoh, 1986; Kanno, Sakuma, Muromachi, & Watanabe, 1988). However, very few studies have focused on the quenching sensitivity of the lower copper and magnesium containing alloys because of their usage for structural components with high strength, and most of the past studies have used only the fast quenching method like water quenching. On the other hand, from our recent results, there is a possibility to lower the quenching sensitivity of 2000 series alloys with lower alloying elements. In this paper, the effect of the copper and magnesium contents with lower alloying elements and quenching rate, especially in case of slower quenching rate than conventional quenching method, on the age hardening behavior of the 2000 series alloys is investigated by the hardness measurement, structure observation and thermal analysis.

## **EXPERIMENTAL PROCEDURES**

Six 2000 series alloys that have a copper content of 2.0-4.0%, and a magnesium content of 0.5-1.5% (mass%, shown in Table 1) were manufactured and studied. Alloy 4.0Cu-1.5Mg had almost the same chemical composition as the AA2024 alloy. These alloys were cast in 90 mm diameter ingots and were homogenized at  $470^{\circ}$ C for 8 h. The ingots were extruded into bars that had a 35 mm width and 3mm thickness at 500°C. These extrusions were solution treated at  $500^{\circ}$ C for 1 h and quenched to room temperature by three quenching methods; i.e., water quenching (WQ) as the fastest, air cooling (AC) as the middle, and furnace cooling (FC) as the slowest. Each quenching rate is shown in Table 2. Immediately after quenching, artificial age hardening was conducted at  $190^{\circ}$ C.

Table 1. Chemical composition of specimens (mass%)									
Alloy	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
1.0Cu-0.5Mg	0.07	0.15	0.96	0.62	0.47	< 0.01	< 0.01	< 0.01	Bal.
1.0Cu-1.5Mg	0.07	0.14	0.98	0.62	1.43	< 0.01	< 0.01	< 0.01	Bal.
2.0Cu-0.5Mg	0.07	0.15	1.94	0.62	0.48	< 0.01	< 0.01	< 0.01	Bal.
2.0Cu-1.5Mg	0.07	0.15	1.99	0.61	1.47	< 0.01	< 0.01	< 0.01	Bal.
4.0Cu-0.5Mg	0.07	0.14	3.85	0.61	0.47	< 0.01	< 0.01	< 0.01	Bal.
4.0Cu-1.5Mg	0.07	0.14	3.95	0.61	1.46	< 0.01	< 0.01	< 0.01	Bal.

Table 2 (	Quenching	rate of e	ach quenc	hing meth	nd average	rate from	500°C to	100°C
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Quenching method	Quenching rate (°C/s)
Water quenching (WQ)	approx. 30
Air cooling (AC)	1
Furnace cooling (FC)	0.008

Scanning electron microscope (SEM) observations were obtained to observe the precipitates under the as-quenched conditions. The age hardening behavior was investigated by Vickers hardness and electrical conductivity measurements after each artificial aging treatment. The precipitation phases were observed after the ageing by a transmission electron microscope (TEM) to know mainly the shape and size of the precipitates and differential scanning calorimetry (DSC) to know the type of precipitates. Each DSC peak and precipitation phase (I: GP (GPB) dissolution, II: S'(S) formation, III: S' (S) dissolution, IV:  $\theta'$  ( $\theta$ ) formation, V:  $\theta'$  dissolution, VI:  $\theta$  dissolution) were cited from prior studies (Starink & Mourik, 1992; Gao, Davin, Wang, Cerezo, & Starink, 2002; Starink, Gao, Davin, Yan, & Cerezo, 2005). For further discussion later on about precipitation behaviors, CCT diagrams were calculated using JMatPro software.

# RESULTS

#### SEM Images and Electrical Conductivity Under As-Quenched Conditions

The SEM images are shown in Figure 1. The electrical conductivity (%IACS) of each specimen in the as-quenched condition is also shown in the figure. For alloys 1.0Cu-0.5Mg, 1.0Cu-1.5Mg, 2.0Cu-0.5Mg, and 2.0Cu-1.5Mg, the difference in the precipitation condition during quenching was minor between each quenching method. Even for the FC, the slowest quenching method, coarse precipitations were rarely observed. Changes in the electrical conductivity were also small, especially the difference between the WQ and AC was only a few percent. On the other hand, for 4.0Cu-0.5Mg and 4.0Cu-1.5Mg, many coarse precipitations in the grain boundaries and inside the grains were observed as the quenching rate of each quenching method decreased. Changes in the electrical conductivity also increased. The difference between the WQ and FC was more than the rest of unit 10% IACS.



Figure 1. SEM images of specimens in the as-quenched conditions. The white particles in the images represent the precipitates. The electrical conductivity of each condition is indicated in the lower right of each image

#### Vickers Hardness

The hardness measurement results are shown in Figure 2. First, the hardness under the as-quenched conditions decreased in the following order: AC > WQ > FC. The age hardening behavior at 190°C was in two steps for the WQ and AC in the 1.0Cu-0.5Mg, 1.0Cu-1.5Mg, 2.0Cu-0.5Mg and 2.0Cu-1.5Mg alloys. The peak hardness of AC was almost the same or slightly higher compared to the WQ. The aging time until the peak aging was 70–100 h for alloys 1.0Cu-0.5Mg and 1.0Cu-1.5Mg, and 20–50 h for alloys 2.0Cu-0.5Mg and 2.0Cu-1.5Mg. The aging rate for the AC specimens was slower than that of the WQ ones. For the specimens containing a higher copper content as the conventional 2000 series alloys, only 4.0Cu-0.5Mg showed a similar aging behavior for the WQ and AC although the peak hardness of AC was significantly lower than that of the WQ. The hardness of 4.0Cu-1.5Mg in the AC showed little change from the first stage of aging (from the as-quenched conditions to less than 10 h) and the difference in the hardness values between the WQ and AC was more than 20. For this specimen. The aging time until the peak aging was 20 h for the WQ specimens and 5–10 h for the AC specimens. The aging time until over-aging for the AC was shorter than for the WQ. All the FC specimens showed little or no changes from the first stage of aging, thus age hardening of these specimens was not recognized.



Figure 2. Vickers hardness after artificial aging at 190°C

## **Electrical Conductivity**

The electrical conductivity measurement results are shown in Figure 3. The electrical conductivity of the WQ and AC specimens increased as the aging proceeded, and changes in this value increased especially for the higher copper-containing specimens. The FC specimens showed a slight increase while no age hardening was recognized.



Figure 3. Electrical conductivity after artificial aging at 190°C

## **TEM Observations**

TEM images of the WQ and AC specimens after artificial aging at  $190^{\circ}$ C are shown in Figure 4. The dot-shape or fine rod-shape GPB zone and fine lath-shape S' phase with a length of about 0.2 µm were observed in the WQ. These precipitates decreased in the AC specimens and many coarse lath-shape S' phases were instead observed. Furthermore, dislocation loops and S' precipitation on the loops that were identified in prior reports (Silcock, Heal, & Hardy, 1953; Silcock, 1960) were also observed in the WQ specimens of the 1.0Cu-0.5Mg, 2.0Cu-0.5Mg and 4.0Cu-0.5Mg alloys.



Figure 4. TEM images of (100), aged at 190°C for 8 h

# **DSC** Analysis

The DSC results are shown in Figure 5. For all the specimens, an endothermic peak at around  $220-250^{\circ}$ C, derived from the dissolution of the GP zone or GPB zone, was identified. Overall, the WQ specimens showed a higher endothermic change than the AC ones, although the 1.0Cu-0.5Mg, 1.0Cu-1.5Mg, 2.0Cu-0.5Mg alloys had little difference between the WQ and AC. However, for the 4.0Cu-0.5Mg and 4.0Cu-1.5Mg alloys, the height of the endothermic peak of the AC was less than half of that of the WQ. At around 300–350°C, exothermic peaks were identified. These peaks were derived from the precipitations of the  $\theta$ ' phase or  $\theta$  phase for the 4.0Cu-0.5Mg, and from the S' phase or S phase for the other specimens. The peak height of the AC specimens was lower than that of the WQ ones.



Figure 5. DSC analysis, aged at 190°C for 8 h

#### DISCUSSION

#### Precipitation Phases During Quenching and Artificial Aging

As already mentioned, a different exothermic peak was identified depending on copper and magnesium content, especially for 2.0Cu-0.5Mg and 4.0Cu-0.5Mg. However, it is difficult to know completely what the precipitation phase of each alloy is, thus precipitation phases and processes are summarized as follows for further discussion. As Sato, Kitaoka, and Kamio mentioned in 1988, the precipitation sequence of the 2000 series alloys that contain copper and magnesium are classified as follows:

$$\alpha \rightarrow GP(1) \rightarrow GP(2) \rightarrow \theta' \rightarrow \theta \tag{1}$$

$$\alpha \rightarrow \text{GPB} \rightarrow \text{S}' \rightarrow \text{S} \tag{2}$$

The precipitation process varies depending on the ratio of the copper and magnesium (Cu/Mg). In other words, process (1) proceeds when Cu/Mg>8, both (1) and (2) proceed in parallel when 4 < Cu/Mg < 8, and (2) proceeds when 1.5 < Cu/Mg < 4. In case of Cu/Mg<1.5, it is considered that process (2) also proceeds from the prior study about the Al-Mg-Cu alloys (Sato, 2006). For the alloys in this paper, (1) for 4.0Cu-0.5Mg, (1) and (2) for 2.0Cu-0.5Mg, and (2) for the other alloys are thought to proceed during the quenching and artificial aging based on the above studies.

#### **Precipitation Behavior during Quenching**

To discuss the precipitation behavior during quenching, CCT diagrams for each alloy were calculated using JMatPro (Figure 6). First, for the 1.0Cu-0.5Mg and 2.0Cu-0.5Mg alloys, the quenching curves of the WQ and AC do not pass through the precipitation nose of the stable phases, such as S or  $\theta$ , during the quenching except for the extremely slow quenching method, like the FC, because of their lower copper and magnesium contents. However, the curves of the WQ and AC pass near the precipitation nose of the metastable phases, such as S' and  $\theta$ '. Thus, it is considered that the precipitation of these phases proceeds to the extent that it does not decrease the age hardenability. This is because the size of the precipitation is so fine or the number density is so low that it does not contribute to increasing the hardness due to its lower alloying contents. In addition, 1.0Cu-1.5Mg with WQ shows similar precipitation behaviors to above alloys.

On the other hand, for the rest of the alloys, the quenching curves of WQ and AC pass through or near the precipitation nose of the metastable phases, such as S',  $\theta$ ' and GP. Especially, for the 4.0Cu-1.5Mg alloy, which has chemical components corresponding to A2024, the quenching curve of AC passes near the precipitation nose of the stable phases although it does not directly pass through the nose. Based on this reason, for the higher copper and magnesium-containing alloys, it is considered that coarse precipitation of the stable phases proceeded during the quenching as the quenching rate decreased from the WQ to AC, to FC.



Figure 6. CCT diagrams calculated by JMatPro

#### Age Hardening Behavior of Different Quenching Rate

Based on the previous results, for the specimens containing a higher copper content, like A2024, it is considered that the precipitation of the stable phases (S,  $\theta$ ) and coarse metastable phases (S',  $\theta$ ') proceed during the slower quenching such as the AC. In addition, from the result that the hardness of AC in the as-quenched condition was higher than that of WQ, these precipitated metastable phases seem to provide a slight contribution to increase the hardness from the as-quenched conditions to less than 10 hours in the age hardening behavior. However, as it is significant for 4.0Cu-1.5Mg, subsequent age hardenability of AC significantly decreases compared to the WQ. This is because the solid solution elements in the matrix were depleted due to coarse precipitation of the stable phases and, at the same time, further coarsening of the precipitated metastable phases proceed during aging. On the other hand, for the alloys containing a lower copper content, such as 1.0–2.0%, coarse precipitation of the stable phases does not easily occur during quenching even at the slower quenching rate of the AC. Furthermore, although precipitation of the metastable phases does occur during quenching when passing near the precipitation nose, it is considered that the precipitations were difficult to coarsen because the original amount of the solid solution elements was not large. Especially, for the 2.0Cu-1.5Mg, the following age hardening leads to a precipitation of the GPB zone for the WQ and to the precipitation of S' for the AC. The age hardening behavior of AC is considered as follows: precipitation of the GPB zone in the first stage of aging (from the as-quenched condition to less than 10 hours) is suppressed by S' that has already precipitated during quenching, then age hardening slowly proceeds as the precipitation of the solid solution elements due to coarse precipitation during quenching is low. In addition, for the alloys 1.0Cu-1.5Mg, 2.0Cu-0.5Mg and 2.0Cu-1.5Mg, the peak hardness of the AC was almost at the same level or slightly higher value when compared to WQ. As already mentioned, this is because the precipitated metastable phases, such as S' and  $\theta$ ', were not coarsened and the number density of S' that contributed to increase hardness was high.

### CONCLUSIONS

The effect of the copper and magnesium contents and quenching rate during the quenching on the age hardening behavior of the 2000 series aluminum alloys was investigated. For the higher copper-containing specimens as the conventional 2000 series alloys, like AA2024, precipitation of the stable phases increased as the quenching rate decreased during the as-quenched conditions. As it is already known, the peak hardness after artificial aging of the AC specimens was significantly lower than that of WQ. This was because the amount of the solid solution component decreased as coarse precipitation of the stable or metastable phases proceeded during the AC. On the other hand, for the relatively lower copper-containing alloys, such as 1.0–2.0% Cu, the amount of coarse precipitation was not significantly increased even in the case of the AC. The artificial age hardening behavior of WQ and AC was so similar that the maximum hardness and aging rate had almost the same level. Based on the TEM images and DSC analysis, many parts of the fine precipitates that increased the hardness were thought to be the GPB zone or fine S' phase for the WQ and a relatively coarse S' phase for the AC. From the calculated CCT diagrams, relatively lower copper containing alloys could keep copper and magnesium in the solid solution state during the AC, so they could be quenched at a rather slower quenching rate such as the AC and there was not the significant difference between the hardness of WQ and AC.

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