Proceedings of the 12th International Conference on
Aluminium Alloys, September 5-9, 2010, Yokohama, Japan

pp. 1045-1050

Effects of Cu Addition on Aging Behavior of Al-0.5%Si-0.3%Mg Alloy

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The aging behavior of Al-0.3mass%Mg-0.5mass%Si alloys with or without Cu was investigated at the working temperature of radiators (i.e., 90°C). It was observed that Cu addition was not necessarily effective in strengthening the alloys in the cases where these alloys were aged for a long time at the working temperature of radiators. The Cu-free alloy stored at 90°C for 4300h possessed approximately the same yield strength as the alloy containing 0.5% Cu or 0.8% Cu. In contrast, when the alloys were stored at room temperature or at 180°C, the yield strength of the alloy containing Cu was larger than that of the alloy not containing Cu. Results of DSC analyses and TEM observations showed that the dominant phases in age hardening were as follows: (i) formation of Mg-Si(-Cu) clusters at room temperature, (ii) formation of clusters and β″-phase precipitates at 90°C, and (iii) formation of needle-shaped β″-phase precipitates at 180°C.

Keywords: *heat exchangers, age hardening, precipitates, β″ phase, clusters.*

1. Introduction

Aluminum brazing sheets, which usually consist of Al-Mn series core alloys and an Al-Si filler alloy, are used for automotive heat exchangers. Automotive heat exchangers are generally manufactured by a brazing process, i.e., by heating to approximately 600°C in a nitrogen atmosphere.

Recently, there has been increasing demand for a reduction in the thickness of heat exchanger materials; in order to satisfy this requirement, the material is required to have high strength. Materials for radiators should foremost possess high strength in order to avoid fatigue breakdown. The addition of Mg to Al-Mn core alloys is a potential method for improving the strength of heat exchanger materials; this is because the brazing process serves as the solution heat treatment and results in Mg_2Si precipitation, which leads to age hardening. However, Mg addition has a limitation of the maximum amount to avoid inferior brazability; hence, age hardening should be promoted by some other method. One such method is to simply add Cu, which is known to be a facilitator of age hardening, to the heat exchanger material [1]. Actually, brazing sheets containing Mg and Cu have already been put to practical use in heat exchangers such as radiators [2]. However, the effect of Cu addition on the aging behavior of the materials at the working temperature of radiators, which ranges from room temperature to approximately 90°C, is not entirely clear.

In this study, the aging behavior of Al-0.3mass%Mg-0.5mass%Si alloys with or without Cu was studied. For the sake of simplicity, we used alloys containing only those elements that form aging precipitates. Furthermore, in order to eliminate the influence of diffused Si from the cladding alloy during the brazing process, the specimens did not contain Al-Si filler alloys. The brazing process was replaced with solution heat treatment, i.e., heating the material at 560°C and then quenching it in water. We conducted the aging treatment procedure not only at the working temperature of radiators but also at higher temperatures, in order to account for other types of heat exchangers. On the basis of the results of this experiment, we discussed the aging phenomena and the effects of alloy composition.

2. Experimental procedure

The chemical compositions of the laboratory-made alloys containing different amounts of Cu are listed in Table 1. An Al-0.3%Mg-0.5%Si alloy in which Cu has not been added is termed the 0%Cu alloy. When 0.5%Cu and 0.8%Cu are added to the 0%Cu alloy, then the resultant alloys are termed 0.5%Cu and 0.8%Cu alloys, respectively. Each of these alloys was homogenized for 8h at 560°C after casting. The alloys were hot- and cold-rolled into 1-mm-thick plates. Tensile specimens with a width of 25 mm and a gauge length of 50 mm were machined from these plates. The direction of the tensile stress was parallel to the rolling direction. The specimens were heated in a salt bath at 560°C for 10min and quenched in water for the purpose of solution heat treatment. After this, they were stored at room temperature (RT), 90°C, and 180°C. The aged specimens were tensile tested at an initial strain rate of 3.3×10^{-3}/s. Differential scanning calorimetry (DSC) analyses were carried out on the materials at a heating rate of 40°C/min. Foil specimens were electrolytically polished using a twin-jet method and then observed by transmission electron microscopy (TEM) at an accelerating voltage of 200 kV.

Table 1 Chemical composition of laboratory-made alloys (mass%).

	Si	Fe	Mg	Cu	Al
0%Cu	0.50	0.13	0.30	Tr.	Bal.
0.5%Cu	0.51	0.12	0.28	0.50	Bal.
0.8%Cu	0.50	0.13	0.29	0.82	Bal.

3. Results

3.1 Aging behavior at RT

Figure 1 shows the yield strength of the alloys containing different amounts of Cu and aged at RT. It is observed that for a high amount of added Cu, the rate of increase in the yield strength is high; further, after 4300 h (i.e., half a year), the strength of the material increases with the amount of added Cu.

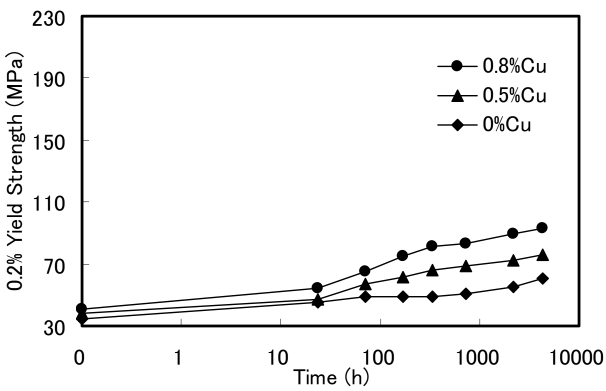

Fig. 1 Yield strength vs. aging time curves of the alloys aged at RT.

TEM images of the 0%Cu and 0.8%Cu alloys aged at RT for 4300 h, as shown in Fig. 2, reveal that both these alloys have no aging precipitates. This indicates that the age hardening is due to the formation of clusters without a rule structure; these clusters probably consist of Si and Mg and may be with or without Cu. DSC analyses were carried out to estimate the amount of clusters (Fig. 3). The resultant curves for all three alloys have endothermic peaks in the temperature range of approximately 180–280°C. The endothermic heat was produced by the decomposition of the aging clusters into the matrix. Figure 4 shows the amount of endothermic heat produced for the corresponding DSC curve shown in Fig. 3. This heat increases with the amount of added Cu. This behavior indicates that the dispersion density of the clusters formed at RT increases with the amount of added Cu.

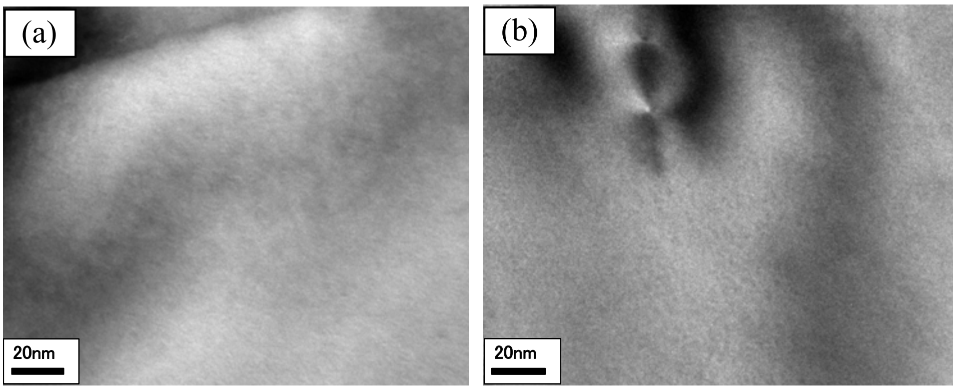

Fig. 2 TEM images of the 0%Cu alloy-(a) and 0.8%Cu-alloy-(b) aged at RT for 4300h.

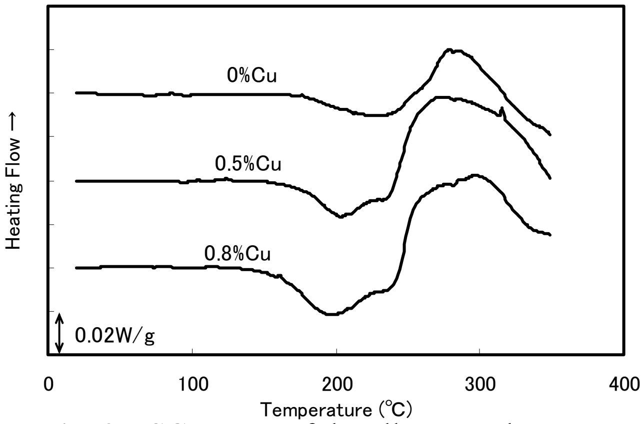

Fig. 3 DSC curves of the alloys aged at RT for 4300h.

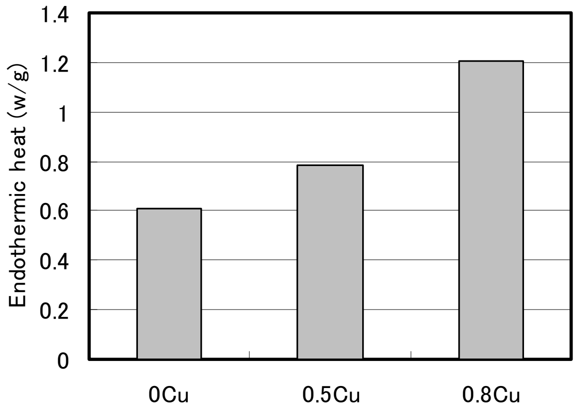

Fig. 4 The amount of endothermic heat of the alloys aged at RT for 4300h. (Refer to Fig. 3)

3.2 Aging behavior at 90°C

Figure 5 shows the yield strength of the alloys aged at 90°C. Although the rate of increase in the strength of the alloys grows with the amount of added Cu, this strength is almost the same for the three alloys aged for 4300h.

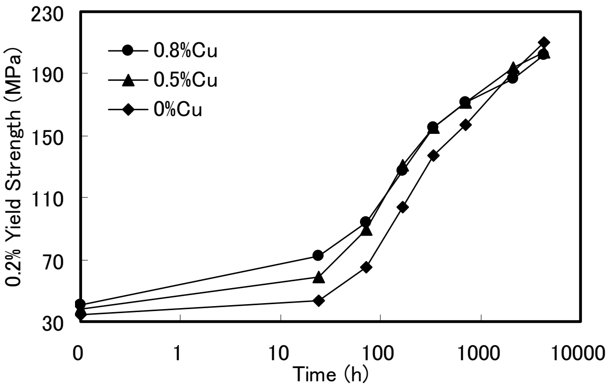

Fig. 5 Yield strength vs. aging time curves of the alloys aged at 90°C.

Figure 6 shows the TEM images of the 0%Cu and 0.8%Cu alloys aged at 90°C for 720h. The 0%Cu alloy has minute spherical precipitates, which are probably an early β″ phase, whereas the 0.8%Cu alloy does not have definite precipitates. The 0.8%Cu alloy that is in the process of aging for 720h possesses high strength in spite of the absence of spherical precipitates; therefore, the clusters are probably dominant in age hardening when the alloys begin aging at 90°C. TEM images of the alloys aged for 4300h are shown in Fig. 7; these images indicate that the 0%Cu alloy has needle-shaped β″-phase precipitates. The 0.8%Cu alloy does not have needle-shaped precipitates, although it has spherical precipitates.

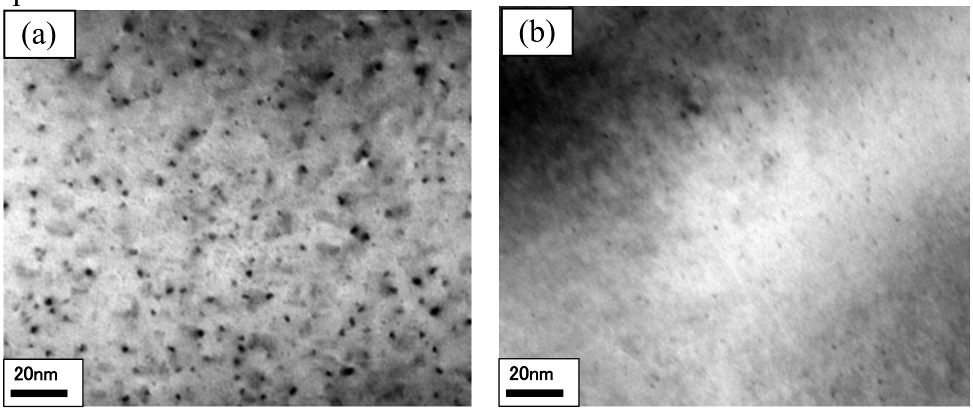

Fig. 6 TEM images of the 0%Cu alloy-(a) and 0.8%Cu-alloy-(b) aged at 90°C for 720h.

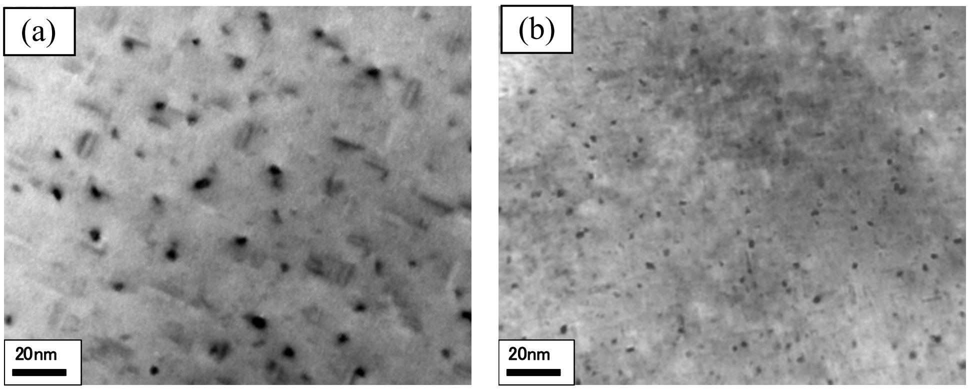

Fig. 7 TEM images of the 0%Cu alloy-(a) and 0.8%Cu-alloy-(b) aged at 90°C for 4300h.

Figure 8 shows the DSC curves of the alloys aged at 90°C for 720h and 4300h. All the curves have endothermic peaks that correspond to the decomposition of precipitates or clusters; the amount of endothermic heat for the respective DSC curves is shown in Fig. 9. Although the amount of endothermic heat increases with the Cu addition for 720h of aging, the amount of heat is highest for the 0%Cu alloy for 4300h of aging.

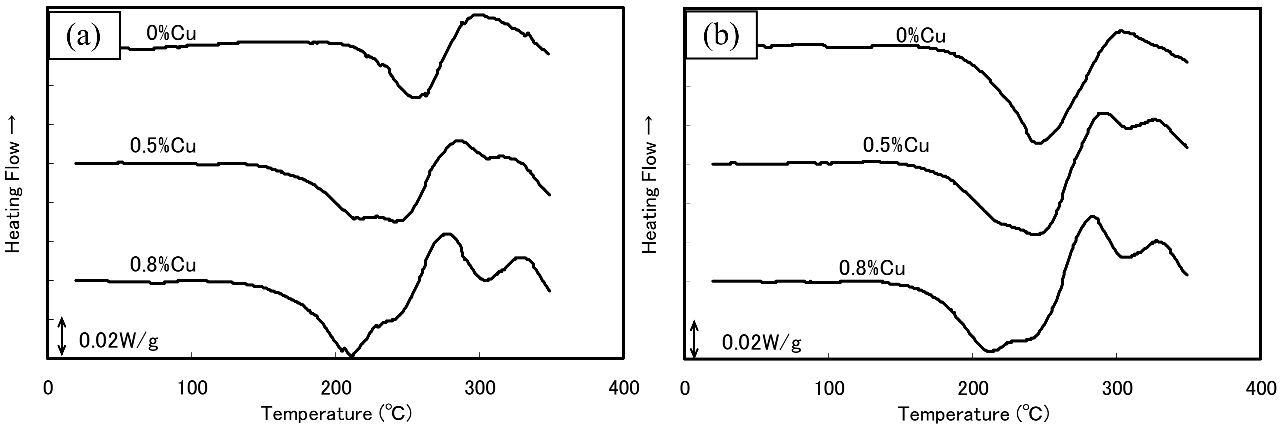

Fig. 8 DSC curves of the alloys aged for 720h-(a) and 4300h-(b) at 90°C.

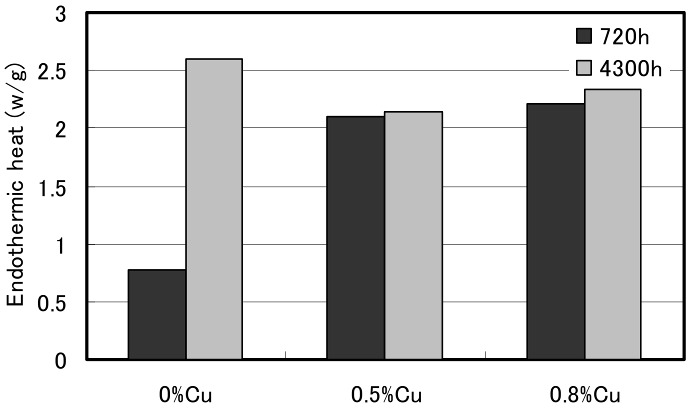

Fig. 9 The amount of endothermic heat of the alloys aged at 90°C. (Refer to Fig. 8)

These results indicate that the dispersion density of clusters increases with the amount of added Cu when the alloy is aged for 720h; further, these results indicate that the β″-phase precipitates of the 0%Cu alloy transit to a more stable state when the alloy is aged for 4300h. In other words, the transformation of the clusters to β″-phase precipitates at 90°C is inhibited by Cu addition.

3.3 Aging behavior at 180°C

Figure 10 shows the yield strength of the alloys aged at 180°C. With increase in the amount of added Cu, the rate of increase in the yield strength grows and the peak strength increases.

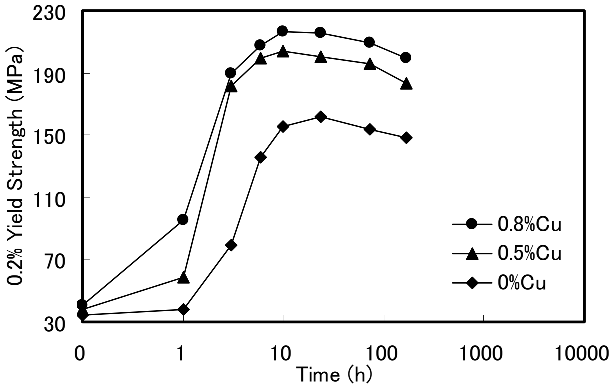

Fig. 10 Yield strength vs. aging time curves of the alloys aged at 180°C.

Figure 11 shows the TEM images of the 0%Cu and 0.8%Cu alloys aged at 180°C for 170h. Needle-shaped β″-phase precipitates are observed in both alloys, and the dispersion density is observed to be larger in the 0.8%Cu alloy than in the 0%Cu alloy. In other words, formation of β″-phase precipitates is promoted by Cu addition. These results are in agreement with those of a previous study that investigated the effects of Cu addition on aging at 175°C [1].

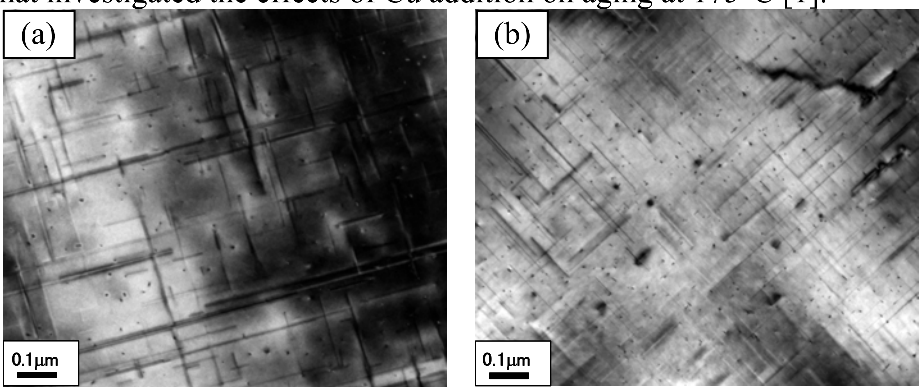

Fig. 11 Transmission electron micrographs of the 0%Cu alloy-(a) and 0.8%Cu-alloy-(b) aged at 180°C for 170h.

4. Discussion

As mentioned above, it was revealed that the effects of Cu addition on the aging behavior were different at different temperatures. For the alloys aged at RT, Cu addition plays an important role in age hardening as it facilitates an increase in the dispersion density of clusters. The transformation from clusters to the β″ phase does not occur.
In contrast, the strengths of the three alloys aged at 90°C for a long time were almost the same irrespective of the amount of added Cu, although the rate of increase in strength grew with the amount of added Cu. The phase transformation of the alloy at 90°C is considered to be as follows. At the beginning of aging, the alloy containing Cu exhibits greater age hardening; this is because the formation of clusters, which is promoted by Cu addition, is dominant at this stage. However, after aging for a long time, the yield strength is almost the same for all three alloys irrespective of the amount of added Cu; this is because the effect of β″-phase precipitates, which are inhibited by Cu addition, becomes greater.
Moreover, the peak strength of the alloys aged at 180°C increased with the amount of added Cu. It has been reported that clusters are also formed at 180°C at a very early stage of aging and are transformed to the β″-phase precipitates [3]. Thus, the difference between the aging behavior at 90°C and that at 180°C is attributed to the difference between the effects of the Cu addition on the transformation from the clusters to the β″-phase precipitates in each case. Although this transformation is inhibited by Cu addition at 90°C, it is not inhibited at 180°C.
As we usually evaluate the strength of a brazed material aged at RT, it has been considered that Cu addition is highly effective in the strengthening of materials. Considering the age hardening that occurs when these materials are used in cars, it can be assumed that Cu addition remains effective even at a working temperature of approximately 180°C. However, it was found that Cu addition was not necessarily effective in increasing the strength of the alloys in the cases where these alloys were aged for a long time at 90°C, which is the working temperature of radiators.

5. Summary

The aging behavior of Al-0.3mass%Mg-0.5mass%Si alloys with or without Cu was investigated, and the following conclusions were drawn:

1. The Cu-free alloy that was stored at 90°C for 4300h possessed approximately the same yield strength as the alloys containing 0.5% Cu or 0.8% Cu.
2. The alloys containing 0.5% Cu or 0.8% Cu that were stored at RT or 180°C possessed larger yield strength than the alloy without Cu.
3. It was indicated that Cu addition was not necessarily effective in strengthening the alloy in the cases where these alloys were aged for a long time at the working temperature of radiators.

References

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