Effect of Sn Addition on the Two-Step Aging Behavior in Al-Mg-Si Alloys for Automotive Application

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Abstract

Aluminum alloys of the 6xxx series which contain excess Si or Cu are well used for the automotive applications because of the high age-hardening response. The effect of addition of small amount of Sn on the two-step aging behavior in 1.2%Mg₂Si-0.5%Si in excess alloy and 1.2%Mg₂Si-0.7%Cu alloy was investigated by means of hardness measurement, differential scanning calorimetry, and transmission electron microscopy. G.P. I zone formation in these alloys aged at 25°C was suppressed by the addition of Sn. The Sn addition to Cu added balanced alloys rather than to excess-Si alloy was effective to suppress the negative effect of the two-step aging.

1. Introduction

In recent years, aluminum alloys of the 6xxx series have found increasing use as age-hardenable materials for automotive body sheets to reduce the weight of automobiles. The 6xxx series alloys which contain excess Si or Cu are widely used for automotive applications because of the high age-hardening response at paint baking process. However, the age-hardening response is decreased when the alloys receive the aging at room temperature before the paint baking. In order to obtain high age-hardening response, it is important to suppress the natural aging. Muromachi et al. [1-2] reported that small amount of Sn addition to the 6xxx series alloys suppresses the natural aging. The purpose of this study is to investigate the effect of Sn addition on the two-step aging behavior in $1.2\%Mg_2Si-0.5\%Si$ alloy and $1.2\%Mg_2Si-0.7\%Cu$ alloy.

2. Experimental Procedures

In order to investigate the effects of Sn addition on the two-step aging behavior in exess-Si alloy and Cu added balanced alloy, the alloys given in Table 1 were melted in air, homogenized in air at 530°C for 13 hours, hot and cold rolled to 1 mm thick sheets. The alloy sheets were solutionized at 550°C for 30 minutes, quenched into water and successively pre-aged at 25°C. Each pre-aged specimen was then aged at 175°C corresponding to the paint baking temperature.

Alloy	Mg	Si	Cu	Sn	AI	Mg₂Si	Excess Si
A	0.79	1.03	-	-	Bal.	1.23	0.59
В	0.78	0.44	0.73	-	Bal.	1.21	0.01
С	0.76	0.96	-	0.10	Bal.	1.18	0.54
D	0.78	0.44	0.69	0.13	Bal.	1.21	0.01

Table 1: Chemical composition of the alloys (mass%).

These specimens are tested for hardness under the load 1kg by a Vickers microhardness tester and for the thermal properties by differential scanning calorimetry (DSC). Microstructures of the specimens aged at 175°C for 5h after pre-aging at 25°C for 3h, and electropolished to thin foils were examined by transmission electron microscopy.

3. Results and Discussion

3.1 Two-Step Age Hardening Curves

Figure 1 shows the two-step age hardening curves at 175°C in the alloys A,B,C, and D in Table 1 when the alloys were pre-aged at 25°C for 1 and 25 days. The maximum hardness alloy A(1.2%Mg₂Si-0.5%Si) is almost equal to that of the of the allov B(1.2%Mg₂Si-0.7%Cu). The hardness of the alloy A(1.2%Mg₂Si-0.5%Si) and the alloy B(1.2%Mg₂Si-0.7%Cu) as pre-aged increased with pre-aging time before the aging at 175°C, and then the delay of age-hardening response at 175°C was occurred. When the alloy A(1.2%Mg₂Si-0.5%Si) and the alloy B(1.2%Mg₂Si-0.7%Cu) was pre-aged, the increase in hardness by the aging for about 30 minutes corresponding to the bake hardening treatment was not obtained. But the hardness of the allov D(1.2%Mg₂Si-0.7%Cu-0.1%Sn) was not increased after pre-aged even for 25 days and the delay of the age-hardening response at 175°C was not observed. On the other hand, the hardness of the alloy C(1.2%Mg₂Si-0.5%Si-0.1%Sn) was increased after pre-aged only for 1 day and the delay of the age hardening response at 175°C was occurred.

3.2 Bake Hardening Response in the Excess-Si Alloy

The bake hardening response was investigated in detail by hardness measurement. The aging at 175°C for 30 minutes is named hereafter the bake hardening treatment. Figure 2 (a) and (b) show the changes in the hardness of the alloy A(1.2%Mg₂Si-0.5%Si) and the alloy C(1.2%Mg₂Si-0.5%Si-0.1%Sn) with the pre-aging time at 25°C, before and after the bake hardening treatment. In the alloy A (1.2%Mg₂Si-0.5%Si), the hardness before the bake hardening treatment increased with increasing pre-aging time. The hardness after the bake hardening treatment markedly decreased when the alloy was pre-aged for more than 3 minutes. On the other hand. in the allov C(1.2%Mg₂Si-0.5%Si-0.1%Sn), the increase of the hardness before the bake hardening treatment was suppressed at the early stage of pre-aging at 25°C, and the hardness after the bake hardening treatment remained even when pre-aged for 3h.



Figure 1: Two-step age hardening curves at 175°C in alloy A(1.2%Mg₂Si-0.5%Si), B(1.2%Mg₂Si-0.7%Cu), C(1.2%Mg₂Si-0.5%Si-0.1%Sn), and D(1.2%Mg₂Si-0.7%Cu-0.1%Sn) when the alloys were pre-aged at 25°C for 1 and 25 days.



Figure 2: Changes in the hardness of the alloy $A(1.2\%Mg_2Si-0.5\%Si)$ and the alloy $C(1.2\%Mg_2Si-0.5\%Si-0.1\%Sn)$ with the pre-aging time at 25°C, before and after the bake hardening (BH) treatment.

3.3 Bake Hardening Response in the Cu Added Balanced Alloy

Figure 3 (a) and (b) show the changes in the hardness of the alloy $B(1.2\%Mg_2Si-0.7\%Cu)$ and the alloy $D(1.2\%Mg_2Si-0.7\%Cu-0.1\%Sn)$ with the pre-aging time at 25°C, before and after the bake hardening treatment.



Figure 3: Changes in the hardness of the alloy $B(1.2\%Mg_2Si-0.7\%Cu)$ and the alloy $D(1.2\%Mg_2Si-0.7\%Cu-0.1\%Sn)$ with the pre-aging time at 25°C, before and after the bake hardening treatment.

In the alloy B(1.2%Mg₂Si-0.7%Cu), the hardness before the bake hardening treatment increased gradually with increasing pre-aging time. The hardness after the bake hardening treatment decreased when the alloy was pre-aged for more than 1h. However, in the alloy D(1.2%Mg₂Si-0.7%Cu-0.1%Sn), the increase of the hardness before the bake hardening treatment was completely suppressed, and the hardness after the bake hardening treatment remained even when pre-aged for 24h. Since the hardness of the alloy D(1.2%Mg₂Si-0.7%Cu-0.1%Sn) after the bake hardening treatment was lower than that of the alloy B(1.2%Mg₂Si-0.7%Cu), Sn addition seems to also suppress the aging during the bake hardening treatment.

The addition of Sn suppressed the natural aging in these alloys. This phenomenon seems to be explained as follows. Sn atoms interact with vacancies more strongly than the solute atoms, Mg, Si, Cu [3], and so trap quenched-in vacancies in the Al-Mg-Si(-Cu) alloys, and reduce the amount of free vacancies which are the carriers of solute atoms. This means that the diffusion of solute atoms is delayed and then precipitation during the natural aging is suppressed. This model has been previously applied to explain the effect of Sn addition on the aging behavior in Al-Cu alloys [4-5]. Positron annihilation experiments suggested the strong interaction between Sn atoms and vacancies in Al-Cu alloys [6]. Muromachi et al. have also applied this model to explain the delay of the aging in Al-1.3%Mg₂Si alloy by the addition of Sn[1-2].

In the present study, the effect of Sn addition on the natural and two-step aging behaviors in excess-Si alloy was found to be different from that in Cu added balanced alloy. This result seemed to be caused by the difference in the concentration of precipitates formed during the aging at 25°C between the alloy C(1.2%Mg₂Si-0.5%Si-0.1%Sn) and the alloy D(1.2%Mg₂Si-0.7%Cu-0.1%Sn). Chemical analysis of the precipitates is required to confirm this assumption.

3.4 DSC Analyses

Figure 4 (a) and (b) show the DSC curves for the alloy $A(1.2\%Mg_2Si-0.5\%Si)$ and the alloy $C(1.2\%Mg_2Si-0.5\%Si-0.1\%Sn)$ pre-aged at 25 °C for 3h, before and after the bake hardening treatment. The increase in the hardness of the alloy $A(1.2\%Mg_2Si-0.5\%Si)$ by the bake hardening treatment was very small at this pre-aging condition. Based on the past findings [7-8], the precipitation process of Al-Mg-Si alloys was assumed to be a

supersatulated solid solution, G.P. I zone, intermediate phase β ", intermediate phase β ', and equilibrium phase β . The peaks on the DSC curve were associated with these precipitate phases in the increasing temperature.



Figure 4: DSC curves for the alloy A(1.2%Mg₂Si-0.5%Si) and the alloy C(1.2%Mg₂Si-0.5%Si-0.1%Sn) pre-aged at 25°C for 3h, before and after the bake hardening treatment. **K**: formation of G.P. I zone, **L**: dissolution of G.P. I zone, **P**: formation of β " phase, **Q**: formation of β ' phase.

In the alloy A(1.2%Mg₂Si-0.5%Si), the peak L corresponding to the dissolution of G.P. I zone was observed in the DSC curve before and after the bake hardening treatment. The height of peak P corresponding to the precipitation of β " phase in the DSC curve before the bake hardening treatment was not so different from that after the bake hardening treatment. This result seems to be explained as follows. G.P. I zones formed during the pre-aging at 25°C are stable enough to remain during the bake hardening treatment. The formation of G.P. I zone reduces the amount of Mg and Si in solid solution, and decreases the amount of β " phase precipitated during the bake hardening treatment [9]. In the alloy C(1.2%Mg₂Si-0.5%Si-0.1%Sn), the peak L was not observed in the DSC curve before the bake hardening treatment and the height of peak P in the DSC curve after the bake hardening treatment was smaller than that before the bake hardening treatment. This means that the formation of G.P. I was suppressed during the pre-aging at 25°C and the amount of β " phase precipitated during the bake hardening treatment.



Figure 5: DSC curves for the alloy B(1.2%Mg₂Si-0.7%Cu) and D(1.2%Mg₂Si-0.7%Cu-0.1%Sn) pre-aged at 25°C for 24h, before and after the bake hardening treatment. L: dissolution of G.P. I zone, **P**: formation of β " phase.

Figure 5 (a) and (b) show the DSC curves for the alloy B(1.2%Mg₂Si-0.7%Cu) and the alloy D(1.2%Mg₂Si-0.7%Cu-0.1%Sn) pre-aged at 25°C for 24h, before and after the bake hardening treatment. Precipitation behaviors for Al-Mg-Si-Cu alloys has been reported that β " phase precipitated during the aging at 185°C in the Cu added balanced alloys [10] and the Cu atoms did not great influence on the formation of Mg/Si co-clusters during the aging at 70°C[11]. Based on these reports, the endothermic peak observed near 170~270°C and the exothermic peak observed near 280°C in DSC curves are assumed to be associated with the dissolution of G.P. I zone and the precipitation of β " phase, respectively. In the alloy B(1.2%Mg₂Si-0.7%Cu), the peak L corresponding to the dissolution of G.P. I zone was present in the DSC curves before and after the bake hardening. The height of peak P corresponding to the precipitation of β " in the DSC curve before the bake hardening treatment was not so different from that after the bake hardening treatment. In the alloy D(1.2%Mg₂Si-0.7%Cu-0.1%Sn), the peak L was not observed in the DSC curve before the bake hardening treatment and the height of peak P in the DSC curve after the bake hardening treatment was smaller than that before the bake hardening treatment. This result means that the formation of G.P. I zone during the pre-aging at 25°C was suppressed, and the amount of β " phase precipitated during the bake hardening treatment was not decreased.

3.5 Observation of Precipitates Microstructure

In order to observe the difference of the precipitates microstructure by the addition of Sn, transmission electron microscopy was carried out. Figure 6 (a) and (b) show TEM bright field images of the alloy A(1.2%Mg₂Si-0.5%Si) and the allov C(1.2%Mg₂Si-0.5%Si-0.1%Sn) pre-aged at 25°C for 3h and successively aged at 175°C for 5h. Both images were obtained when the electron beam was parallel to the [001] direction of the α -Al parent phase. Needle-shaped precipitates, which are attributed to the β " phase from the DSC analyses, are observed along the <100> directions of the α -Al. The density of the β " precipitates in the alloy C(1.2%Mg₂Si-0.5%Si-0.1%Sn) is higher than that of the alloy A(1.2%Mg₂Si-0.5%Si). The difference in the microstructures of β " precipitates formed during the aging at 175°C after the pre-aging at 25°C by the addition of Sn agrees with the results of hardness measurements and DSC analyses.



Figure 6: TEM bright field images obtained from the alloy $A(1.2\%Mg_2Si-0.5\%Si)$ and the alloy $C(1.2\%Mg_2Si-0.5\%Si-0.1\%Sn)$ pre-aged at 25°C for 3h and successively aged at 175°C for 5h.

4. Summary

The effect of 0.1%Sn addition on the two-step aging behavior in 1.2%Mg₂Si-0.5%Si alloy and 1.2%Mg₂Si-0.7%Cu alloy has been investigated by means of hardness measurement, differential scanning calorimetry, and transmission electron microscopy.

- 1. The natural aging was suppressed and the delay in the bake hardening response was reduced by 0.1%Sn addition in the 1.2%Mg₂Si-0.5%Si and 1.2%Mg₂Si-0.7%Cu alloys.
- 2. This effect of Sn addition was more effective in the 1.2%Mg₂Si-0.7%Cu alloy rather than in the 1.2%Mg₂Si-0.5%Si alloy.

References

- [1] S. Muromachi and T. Mae, Journal of the Japan Institute of Metals, 35, 1021-1027, 1971.
- [2] S. Muromachi and T. Mae, Journal of the Japan Institute of Metals, 38, 130-138, 1974.
- [3] L. Thome and H. Bernas, Hyperfine Interactions, 5, 361-, 1978.
- [4] H. Kimura and R. R. Hashiguti, Acta Metallurgica, Vol.9, 1076-1078, 1961.
- [5] H. Kimura and R. R. Hashiguti, Trans. JIM, Vol.16, 361-368, 1975.
- [6] R. Nagai, S. Tanigawa and M. Doyama, Scripta Metallurgica, Vol.10, 529-531,1976.
- [7] G.B.Burger, A.K.Gupta, P.W.Jeffrey, and D.J.Lloyed, Materials Characterization, 35, 23-39, 1995.
- [8] W.F.Miao and D.E.Laughlin, Scripta Materialia. Vol.40, No.7, 873-878, 1999.
- [9] M. Saga, Y. Sasaki, M. Kikuchi, A. Hibino, and M. Matsuo, Journal of Japan Institute of Light Metals, Vol.53, No.11, 516-522, 2003.
- [10] L. Sagalowicz, G. Hug, D. Bechet, P. Sainfort and G. Lapasset, ICAA-4, Trans Tech Publication, Switzerland, 636-643, 1994.
- [11] G. A. Edwards, K. Stiller, G. L. Dunlop and M. J. Couper, Acta mater. Vol.46, No.11, 3893-3904, 1998.