Proceedings of the 9th International Conference on Aluminium Alloys (2004) 258
Edited by J.F. Nie, A.J. Morton and B.C. Muddle

Bake-Hardenability of Al-Mg-Cu-X (Ag,Zn,Si) Alloy Sheets

Y. Suzuki[1], A. Hibino[1], T. Muramatsu[2], S. Hirosawa[3], T. Sato[3]

[1]Furukawa-SKY Aluminum Corp., Technical Research Division, 1351 Uwanodai, Fukaya-shi, Saitama 366-8511,Japan.
[2]Furukawa-SKY Aluminum Corp., Technical Research Division, 21-1 Kurome, Mikuni-cho, Itai-gun, Fukui 913-8588, Japan.
[3]Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan.

Keywords: Al-Mg-Cu, Al-Mg-Cu-Ag, Precipitation, Age-hardening, Bake-hardening

Abstract

Age-hardening behaviours of Al-3%Mg-1%Cu (in mass%) alloys with and without Ag, Zn and Si were investigated. The Al-Mg-Cu ternary alloy showed two-stage hardening at 170°C; i.e. the first rapid hardening within 2min and the second hardening after 2000min. The addition of 0.4%Ag accelerated the age-hardening in both the stages. Precipitates in the Ag-bearing alloys were much finer than those of the Ag-free alloys after peak-ageing. 0.4%Zn and 0.4%Si additions were less effective than Ag in improving the strengths at shorter ageing times. The yield strength after bake-hardening treatment was improved not only by Ag addition but also by an optimized heat-treatment.

1. Introduction

Al-Mg alloy sheets are utilized in various applications because of their well balanced properties such as mechanical strength, ductility and press-formability. In the application as automotive body sheets, however, unfavourable bake-softening is well-known to occur during paint-baking after press-forming. In contrast, the strength of Al-Mg-Si alloys can be increased during paint-baking by taking advantage of the precipitate hardening. Therefore, Al-Mg alloys will be more fascinating if they possess the bake-hardenability like Al-Mg-Si alloys. Some previous researches [1-3] presented that Cu addition makes Al-Mg alloys bake-hardenable. However, the yield strengths after stretch-baking (BH-YS) of the Al-Mg-Cu alloy sheets were not so high compared with those of advanced Al-Mg-Si alloy sheets (See Table 1).

Table 1: Previously reported data of bake-hardenability of Al-Mg-Cu alloys [1-3]. The comparison with those of some advanced 6XXX alloys for automotive body sheets [4] is also listed. BH: 2% stretching and baking (*170°C,20min, ** 180°C,30min, ***170°C,30min)

Alloy	Composition	T4 tensile properties			BH-YS	Ref.
		UTS [MPa]	YS [MPa]	EL [%]	[MPa]	
Al-Mg-Cu	Al-2.5%Mg-0.5%Cu-(Si)	225	90	30	150*	[1]
	Al-3.6%Mg-1.0%Cu-(Mn)	271	103	34	188*	[2]
	Al-4.2%Mg-0.6%Cu	272	107	30	170**	[3]
6XXX body sheets	Al-Mg-Si	230	120	30	195***	[4]
	Al-Mg-Si-Cu	255	125	31	200***	[4]

In this work, a series of experiments has been conducted to develop Al-Mg-Cu alloy sheets with excellent bake-hardenability. The effects of small amounts of Ag, Zn and Si on the age-hardening behaviour and bake-hardenability of Al-3%Mg-1%Cu (in mass%) alloys has also been investigated.

2. Experimental

Five alloys shown in Table 2 were cast in metal molds, and then hot- and cold-rolled to 1mm thick sheets by using laboratory scale equipments. Solution heat treatment (SHT) was performed in a salt bath mainly at 520°C for 25sec, followed directly by water quenching. Artificial ageing behavior of the T4 sheets (1week storage at R.T. after SHT) was investigated mainly at 170°C, which is a general paint-baking temperature for automotive body sheets. The ageing treatment was given in an oil bath at 170°C for 1-200min or in an electric furnace for longer times than 200min. Micro-hardness test, electrical resistivity measurement, differential scanning calorimetry (DSC) and transmission electron microscopy (TEM) observation were performed. The yield strengths were also measured for the specimens not only aged at 170°C for 20min but also 150°C for 20min to determine the values of BH-YS. The effects of higher SHT temperatures; i.e. 520-560°C for 30min, was also investigated. Note that the procedure of 2% stretching and ageing treatment at 170°C is considered to well correspond to the actual process of press-forming and paint-baking for body sheet materials.

Table 2: Compositions of Al-Mg-Cu-X alloys. [mass%]

Alloy	Mg	Cu	Ag	Zn	Si	Fe	Ti
3Mg-1Cu	3.04	0.97	---	---	0.10	0.12	0.02
3Mg-1Cu-0.2Ag	2.98	0.99	0.20	---	0.10	0.13	0.02
3Mg-1Cu-0.4Ag	2.91	0.99	0.40	---	0.10	0.12	0.02
3Mg-1Cu-0.4Zn	3.01	1.02	---	0.43	0.10	0.13	0.02
3Mg-1Cu-0.4Si	2.93	0.99	---	---	0.39	0.12	0.02

3. Results and Discussion

3.1 Age-hardening Behavior

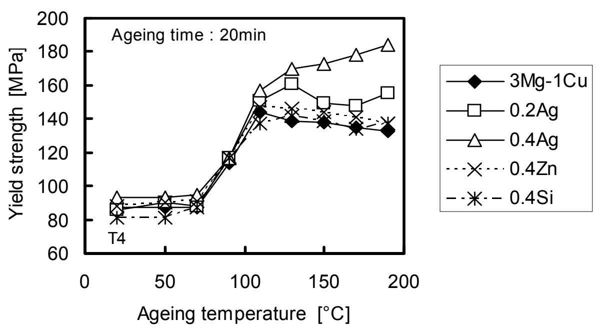

Figure 1: Yield strength - ageing temperature curves of the Al-Mg-Cu-X alloys.

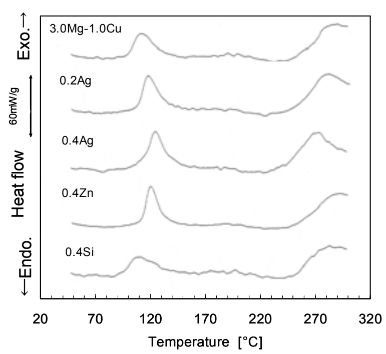

Figure 2: DSC curves of the Al-Mg-Cu-X alloys (Heating rate is 10°C/min).

Figure1 shows the changes in yield strength of the Al-3Mg-1Cu-X alloys aged at various temperatures for 20min. No evident age-hardening occurs at 50-70°C in all the investigated alloys, whereas considerable hardening takes place at temperatures more than 90°C.

From the DSC curves in Figure 2, furthermore, the first exothermic peak was found to form at 90-120°C in all the alloys. This peak is related to the formation of clusters or GPB zones which contribute to the hardening at a general paint-baking temperature of 170°C. On the other hand, the peak at higher temperatures above 250°C originates from the precipitation of S´ or S phase of Al-Cu-Mg alloy system although the formation of different phases is quite probable in the Ag-bearing alloys.

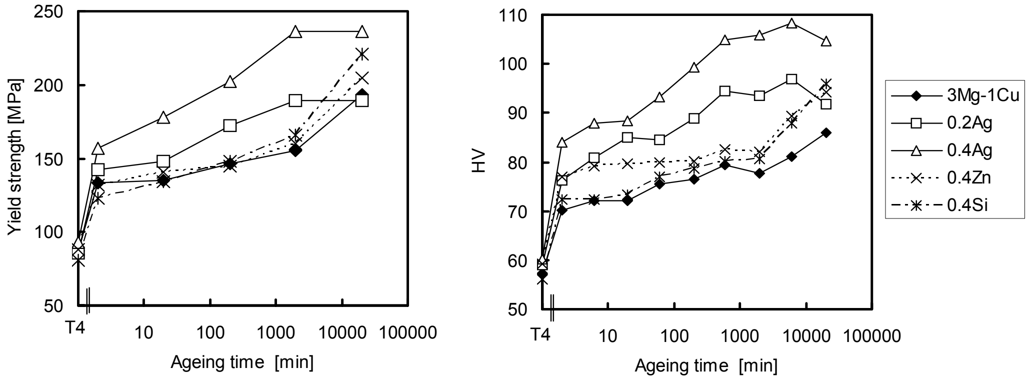

Figure 3: Changes in yield strength and micro-hardness of the Al-Mg-Cu-X alloys aged at 170 °C

The changes in yield strength and hardness of the Al-Mg-Cu-X alloys during ageing at 170°C are shown in Figure 3. The Al-Mg-Cu ternary alloy exhibits two-stage hardening behavior; i.e. the first rapid hardening within 2min and the second hardening from ~2000min.

It should be noted in Fig.3 that the addition of 0.4%Ag accelerates the hardening in both of the stages. When compared with the Ag-free and 0.2%Ag-bearing alloys, the 0.4%Ag-bearing alloy obviously exhibits a faster and larger increases in yield strength and hardness throughout the ageing process. In contrast, the additions of Zn and Si are less effective in increasing the strength than the Ag-bearing alloys until prolonged ageing times.

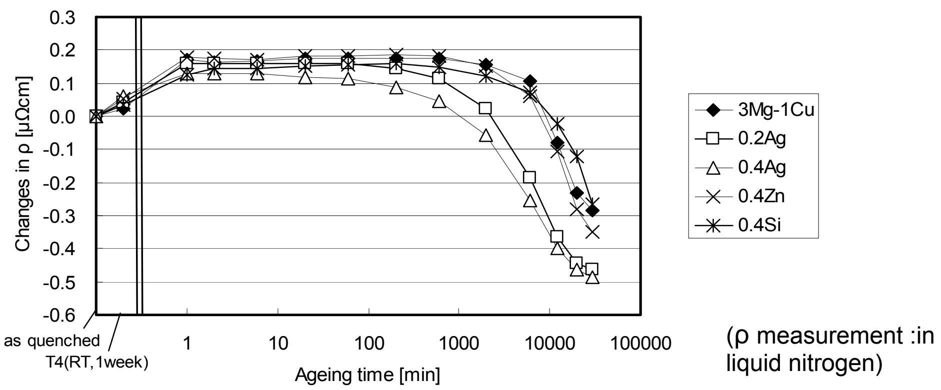

Figure 4: Changes in electrical resistivity ρ of the Al-3Mg-1Cu-X alloys during ageing at 170°C.

The changes in electrical resistivity of the Al-Mg-Cu-X alloys during ageing at 170°C are shown in Figure 4. The resistivity increase occurs within 1min in all the alloys in relation to the age-hardening in the initial stage of ageing. The decrease of the resistivity starts earlier in the Ag-bearing alloys than in the other alloys in consistent with the accelerated hardening to peak hardness by Ag addition.

TEM images of the Al-Mg-Cu-X alloys aged at 170°C for 20000min are shown in Figure 5. There can be seen an obvious microstructural difference between the Ag-bearing alloys and the other alloys. Lath-shaped precipitates of several hundred nanometers in length are seen in the Ag-free alloys, whereas fine equiaxed precipitates with the average diameter of ~15nm are dispersed in the 0.4%Ag-bearing alloy. The coarsened particles in the Ag-free alloys seems to be S-type precipitates (S or S´ phase) as reported in the previous researches for the similar Al-Mg-Cu alloys [5,6]. Note that there may be also retained GPB zones in the microstructure. In contrast, the fine particles in the Ag-bearing alloys are considered to be the same phase as T phase in an Al-4%Mg-1.5%Cu-0.5%Ag alloy [5].

Another possibility of X´ phase [7] may be rejected because the morphology of the particles in the present study is not identical to that of X´, which is reported as hexagonal shaped platelet on {111} [7]. It is interesting to know that both of T and S-type phases co-exist in the 0.2%Ag-bearing alloy with a tendency that the T particles are not so fine as those in the 0.4%Ag-bearing alloy. The coarse and inhomogeneous microstructure in the 0.2%Ag-bearing alloy must be responsible for the lower peak strength than that of the alloy with 0.4%Ag. As for the alloys with Zn and Si, furthermore, the precipitates besides the S-type particles probably form because the higher yield strengths were obtained after prolonged ageing times (Fig.3).

According to the phase diagram of Al-Cu-Mg alloy system at 190°C [4], the composition of the ternary alloy in the present study is included in the region of (α+S+T).

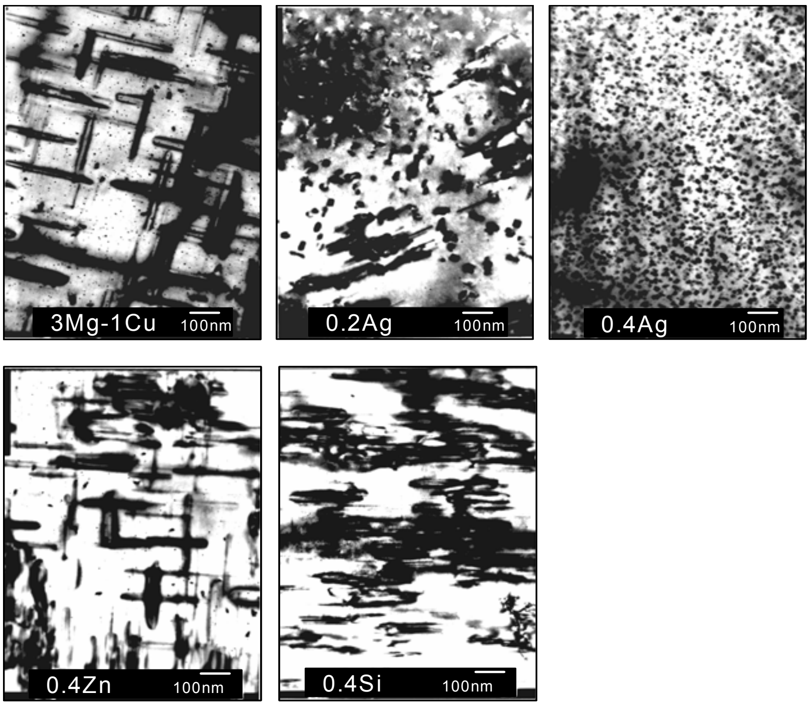

Figure 5: TEM images of the Al-Mg-Cu-X alloys aged at 170°C for 20000min.

Therefore, T phase seems to be formed in all the investigated alloys, especially after prolonged ageing times. However, no T phase was observed even in the ternary alloy, suggesting that Ag plays a role in stabilizing T phase to some extent. In fact, EDX analysis for the 0.4%Ag-bearing alloy revealed that the concentration of Ag in the T particles (or including the adjacent area) is higher than that within the matrix. To understand such an effect of additional elements, the detection of nanoclusters formed in the shorter ageing times is planed by authors using a three-dimensional atom probe (3DAP).

3.2 Bake-hardenability

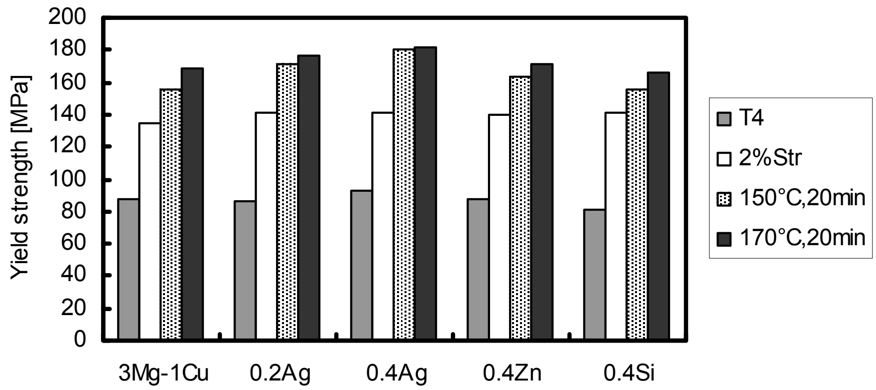

Figure 6:Yield strength before and after stretch-baking (BH-YS) of the Al-Mg-Cu-X alloys (SHT: 520°C, 25sec, Stretching: 2%, Baking: 150°C, 20min or 170°C,20min).

Figure 6 shows the bake hardenability of the Al-Mg-Cu-X alloys sheets. The yield strengths after T4 treatment around 80-90MPa are increasing to ~140MPa by 2% stretching and to over 170MPa by baking at 170°C for 20min. The addition of 0.4%Ag increases the bake-hardenability of Al-Mg-Cu alloys, resulting in the highest BH-YS above 180MPa. The increase in BH-YS by the additions of 0.2%Ag and 0.4%Zn is quite small although the addition of 0.4%Si shows no positive effect on the bake-hardenability. It is noteworthy, furthermore, that baking at 150°C still gives considerable hardening to the alloys. Therefore, this type of bake-hardenable Al-Mg-Cu alloys will be preferable if baking is employed at low temperatures as results of saving energy and optimizing temperatures for water-based paints.

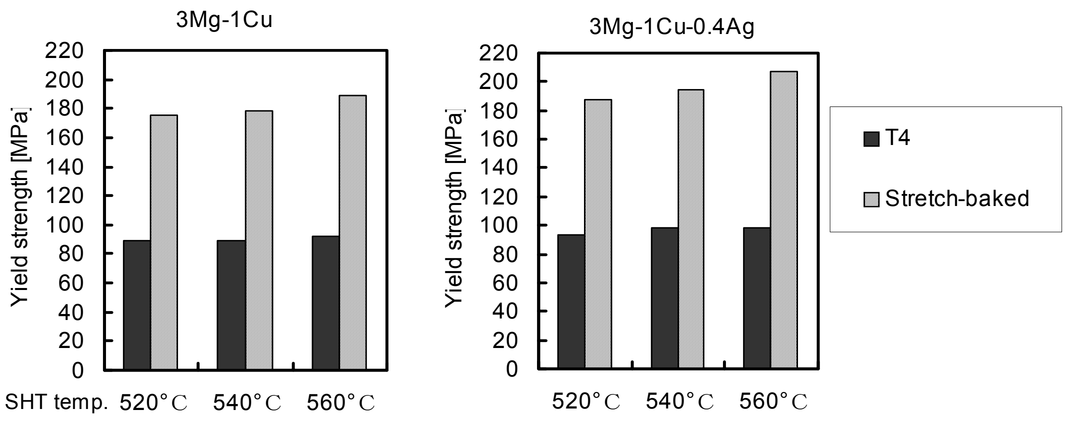

Figure 7: Yield strength after stretch-baking (BH-YS) of the Al-3Mg-1Cu and Al-3Mg-1Cu-0.4Ag alloys. (Stretching: 2%, Baking: 170°C, 20min, SHT:520-560, 30min)

The BH-YS of the advanced Al-Mg-Si alloys for body sheets is ~200MPa, which is higher than that of the Ag-bearing alloys in Figure 6. To achieve further improvement in BH-YS, therefore, additional experiments have been performed. Figure 7 shows the BH-YS of the ternary and 0.4%Ag-bearing alloys solution heat-treated at 520-560°C for 30min. The Higher SHT temperature leads to the higher BH-YS in both alloys. The Ag-bearing alloy with SHT at 560°C shows the highest BH-YS above 200MPa, which is comparable to that of the advanced 6XXX alloy. Note that even in the Ag-free alloys BH-YS reaches 190MPa when SHT is employed at higher temperatures.

4. Conclusions

The investigated Al-3%Mg-1%Cu (in mass%) ternary alloy exhibits two-stage hardening during ageing at 170°C. The addition of 0.4%Ag accelerates and increases hardness and yield strength in both of the stages because of the remarkable change in precipitates. In the T6 condition, the Ag-free alloys contain lath-type precipitates of S or S´, while the Ag-bearing alloys show the denser distribution of fine precipitates of T (or X´). In contrast, the additions of 0.4%Zn and 0.4%Si are less effective than Ag addition to improve the strengths.

The Ag addition is also effective to improve bake-hardenability. The BH-YS of the 0.4%Ag-bearing alloy at 170°C is above 180MPa, which is 15MPa higher than that of the ternary alloy. Considerable bake-hardening is still observed at 150°C in the alloys and the BH-YS above 200MPa is obtained by an optimized SHT condition even for the Ag-free alloys.

Acknowledgements

This study has been conducted in “Nanotechnology Metal Project” supported by New Energy and Industrial Technology Development Organization (NEDO) and The Japan Research and Development Center for Metals (JRCM).

References

[1] T.Fujita, K.Hasegawa, S.Mitano, M.Niikura, T.Koike, M.Funakawa, N.Yoshihara and K.Ohori, Aluminum Applications for Automotive Design, SAE SP-1097, 41, 1995.
[2] Y.Suzuki, M.Matsuo, M.Saga and M.Kikuchi, Proc.ICAA-5, Grenoble, 1789-1794, 1996.
[3] B.Verlinden, P.Ratchev, P.DeSmet and P.Van Houtte, Proc.ICAA-6, Toyohashi, 1075-1081, 1998.
[4] "Aluminum products and the manufacturing technology" ed. By T.Mogi, The Japan Institute of Light Metals, 229, 2001 in Japanese.
[5] J.T.Vietz and I.J.Polmear, J.Inst.Metals, 94, 94, 1966.
[6] P.Ratchev, B.Verlinden, P.DeSmet and P.Van Houtte, Proc.ICAA-6, Toyohashi ,757, 1998.
[7] S.P.Ringer,T.Sakurai and I.J.Polmear, Acta mater. 45, 3731, 1997.