

## EFFECT OF Zn ADDITION ON INTERGRANULAR CORROSION RESISTANCE OF Al-Mg-Si-Cu ALLOYS

Keitarou YAMAGUCHI, and Ken TOHMA

Technical Development Center, Mitsubishi Aluminum Co., Ltd.  
85 Hirimatsu, Susono City, Shizuoka Prefecture, 410-1127, Japan.

**ABSTRACT** The under-paint film corrosion phenomenon and its prevention method for the 6000 series aluminum alloy sheet have been investigated. Cu-containing Al-Mg-Si alloys were susceptible to intergranular corrosion and the corrosion rate significantly increased under the film. The mechanism of the intergranular corrosion was the selective dissolution of the  $Mg_2Si$  phase that precipitated in the grain boundaries. Also the phenomenon was galvanically induced between less noble  $Mg_2Si$  and the noble Cu-containing grain body. A small amount of Zn addition was markedly effective to prevent intergranular corrosion and, therefore, improve the corrosion resistance of a painted sheet.

**Keywords:** *intergranular corrosion, Al-Mg-Si alloy, Cu content,  $Mg_2Si$ , corrosion resistance*

### 1. INTRODUCTION

The 5000 series Al-Mg alloys have mainly been selected from the viewpoint of good formability for automotive body panels, but these alloys have a problem of stretcher strain marks (SSM) after hard forming. Recently, there has been a big demand for the 6000 series Al-Mg-Si alloys because of its age hardening that provides cost reduction, and the prevention of the SSM problem. However, Al-Mg-Si alloys have problems of less phosphatability and corrosion resistance than those of the Al-Mg alloys. Although Cu in the Al-Mg-Si alloy was effective for increasing the forming rate of the zinc phosphate films, the filiform corrosion resistance significantly deteriorated in the alloys containing more than around 0.3%Cu. In these alloys, severe intergranular corrosion was observed under the painted film.

In this paper, the effect of Cu content on the susceptibility to intergranular corrosion of the Al-Mg-Si alloys was investigated. Also a prevention method against intergranular corrosion by Zn addition to the alloys was proposed to improve the corrosion resistance of the painted aluminum sheet.

### 2. EXPERIMENTAL PROCEDURE

#### 2.1 Specimen

The chemical compositions of the alloys are listed in Table 1. After homogenization at 813K for 8 hours, and grinding the surface, the ingots were hot-rolled then cold-rolled into 1mm thick sheets. The sheets were solution treated at 813K for 2 hours and then quenched in water. They were then aged at 443K for 15 minutes (baking treatment), at 473K for 60 minutes to 180 minutes (peak aging), and at 473K for 24 hours (over aging). All specimens were immersed into a 5%  $HNO_3$  solution at 293K for 5 minutes, and then pickled in a 10% NaOH solution at 293K for 3 minutes. After rinsing with water, they were finally passivated in a 5%  $HNO_3$  solution at 293K for 1 minute.

#### 2.2 Electrochemical measurements

The size of the specimen was 150mm long and 70mm wide. Electrochemical polarization measurements were carried out in 2.67%  $AlCl_3$  solution. The polarization curves were potentiodynamically measured with a scanning rate of 0.5mV/s. A saturated calomel electrode (SCE) was used for the reference electrode. Galvanostatic anodic dissolution at 0.3mA/cm<sup>2</sup> was carried out in a solution containing 300ppm  $Cl^-$  ion and 100ppm  $SO_4^{2-}$  ion at room temperature for 24 hours.

### 2.3 Painting

The specimens were treated in a zinc phosphate solution for 2 minutes followed by the cathodic electrodeposition coating ( $20 \mu\text{m}$ ), intermediate coating ( $30 \mu\text{m}$ ) and top coating ( $30 \mu\text{m}$ ).

### 2.4 Evaluation of corrosion resistance

One side of the painted surface was scribed to the depth of the substrate. The conditions of the corrosion test are shown in Table 2. The length of the filiform corrosion was measured after the corrosion test.

Table 1 Chemical composition of specimens.(wt %)

No.	Mg	Si	Cu	Zn	No.	Mg	Si	Cu	Zn
1	0.81	0.82	tr.	tr.	7	0.81	0.83	0.45	tr.
2	0.83	0.80	0.05	tr.	8	tr.	1.05	tr.	tr.
3	0.81	0.83	0.09	tr.	9	0.81	tr.	tr.	tr.
4	0.85	0.85	0.14	tr.	10	0.80	0.83	0.20	0.10
5	0.80	0.81	0.20	tr.	11	0.83	0.79	0.20	0.28
6	0.80	0.81	0.29	tr.	12	0.84	0.80	0.22	0.48

Table 2 Test condition of cyclic corrosion test

step	condition		cycle
1	salt spray	0.5%NaCl,308K,2 hours	120
2	dry	333K,4 hours	
3	humidity	323K,2 hours,RH 95%	

## 3.RESULTS AND DISCUSSION

### 3.1 Mechanism of intergranular corrosion of Al-Mg-Si-Cu Alloys.

Intergranular corrosion susceptibility of various Cu-containing alloy specimens was evaluated by anodic dissolution. The results are shown in Table 3. The alloys containing more than 0.2%Cu were susceptible to intergranular corrosion after the baking treatment for an automotive body at 443K for 20 minutes. Even the 0.05%Cu-containing alloy become susceptible to intergranular corrosion at peak aging. Similar susceptibility results were obtained by the immersion test in 1 ppm  $\text{Cu}^{2+}$  containing tap water at 313K for 7 days, a condition that was closer to the atmospheric environment. As the measurement of the dissolution potential of the phases obtained after baking treatment, electrochemical polarization has proved to be a very useful tool to solve the mechanism of highly selected dissolution like intergranular corrosion. The pitting potential of the specimens listed in Table 3 were measured, and the results are shown in Figure 1. The potential of the solution treated specimens were highly noble due to Cu addition even at a concentration as low as 0.05%. On the other hand, the potential of the baking treated and peak aged specimens were in the range from -710mV to -730mV, independent of Cu content, which were estimated to be the dissolution potential of the grain boundaries.  $\text{Mg}_2\text{Si}$  is a common compound precipitated in the Al-Mg-Si-Cu alloy. To estimate the dissolution potential of the  $\text{Mg}_2\text{Si}$  precipitates, the polarization curve of the Al-4%Mg-1%Si alloy containing coarse  $\text{Mg}_2\text{Si}$  precipitates was measured[1]. The potential of the active dissolution of the  $\text{Mg}_2\text{Si}$  compound was confirmed to be the same as that of the grain boundary corrosion measured in Figure 1. SEM photomicrograph of the morphology of the grain boundary dissolved by anodic dissolution for 1 hour are shown in Figure 2. In the case of the 0.05%Si alloy (b), facet pitting of the precipitation solute depleted type[2] was observed in the vicinity of the grain boundaries. On the other hand, the dotted selective dissolution along the grain boundaries was observed in the Al-Mg-Si alloy(a). From these results, it was suggested that preferential dissolution of  $\text{Mg}_2\text{Si}$  was the cause of the intergranular corrosion of the Al-Mg-Si-Cu alloys.

Table 3 Effect of Cu content and heat treatment on susceptibility to intergranular corrosion after anodic dissolution.

Heat Cu(%) Treatment	Less	0.05	0.09	0.14	0.20	0.29	0.45
As Solutiontreated	○	○	○	○	○	○	○
443K,20min	○	○	○	○	○▲	▲	▲
473K,60min	○▲	●	●	●	●	●	●
473K,180min	○	●	●	●	●	●	●
473K,24hr	○	○	○	○	○	○	○

Corrosion forms: ○Pitting, ▲Slight intergranular corrosion,  
●Well-defined intergranular corrosion

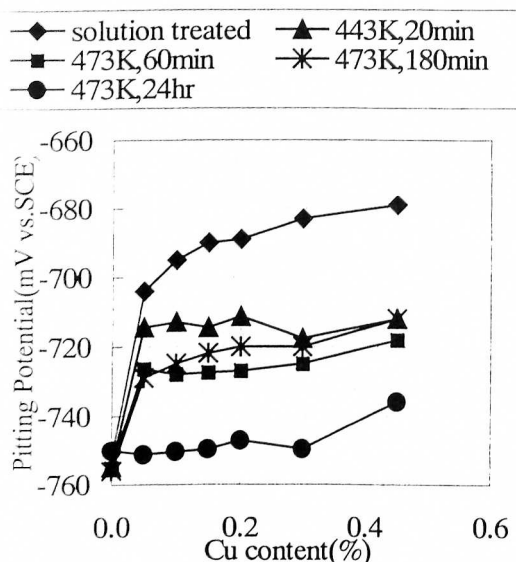


Figure 1 Effect of Cu content and heat treatment on pitting potential of Al-Mg-Si alloy .

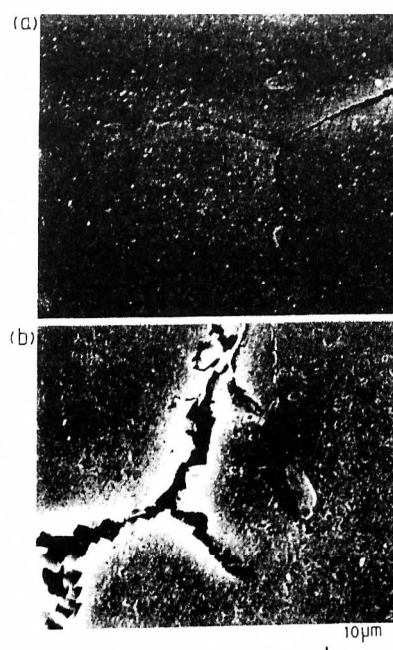


Figure 2 Surface observation on Al-0.8Mg-0.8Si-0.45Cu and Al-1.0Si alloys after anodic dissolution for 2 hours.

Based on the outcome of the test, a schematic representation of the intergranular corrosion mechanism of the Al-Mg-Si-Cu alloys is shown in Figure 3. The pitting potential of the grain bodies become noble by the addition of a slight concentration of Cu. When the alloys are aged, Mg<sub>2</sub>Si precipitates are formed in the grain boundary. The precipitates have a less noble dissolution potential than that of the grain bodies. Accordingly, the susceptibility to intergranular corrosion was induced by the formation of precipitation in the grain boundary. On the other hand, in the over aging treatment, the precipitation also occurs within the grain bodies, which leads to no potential difference between the grain boundary and grain body. In that structure, intergranular corrosion does not occur any more. Based on the discussion, intergranular corrosion can be controlled if the dissolution potential of the grain bodies becomes less noble than that of Mg<sub>2</sub>Si. Zn was selected as the additional element in the alloys because of its potential lowering effect within the solubilities limit.

Table 4 Effect of Zn content and heat treatment on susceptibility to intergranular corrosion after anodic dissolution

Zn(%)	solution treated	443K 20min	473K 60hr	473K 180min	473K 24hr
tr.	○	●	●	●	○
0.60	○	○	●	●	●
1.17	○	●	●	●	●
1.78	○	●	●	●	●

[Evaluation] ○ pitting, ● intergranular corrosion

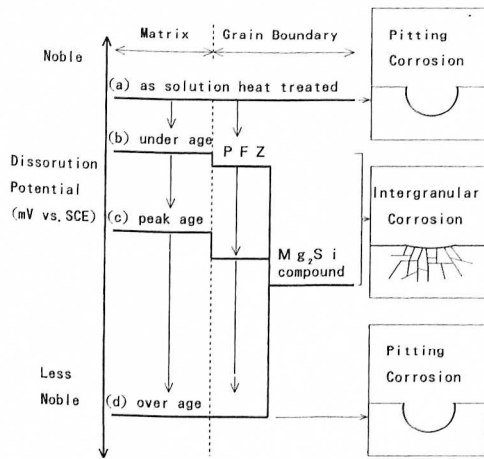


Figure 3 Schematic representation of intergranular corrosion mechanism of Al-Mg-Si-Cu alloy.

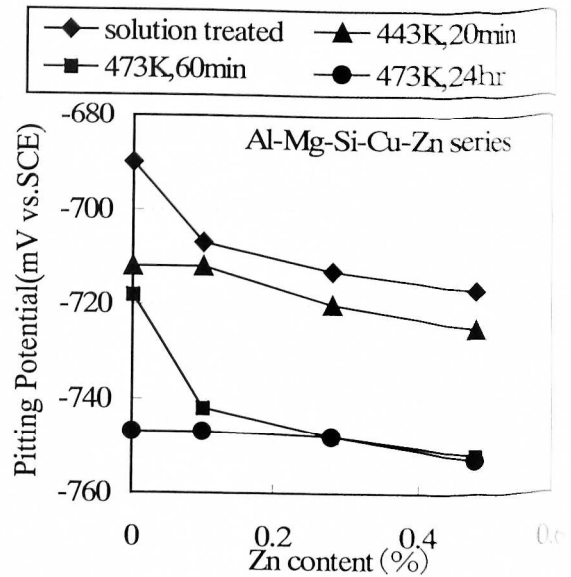


Figure 4 Effect of Zn content and heat treatment of Al-Mg-Si-Cu alloy.

### 3.2 Effect of Zn content

Table 4 shows the effect of Zn content and heat treatment on the susceptibility to intergranular corrosion of the Al-0.8Mg-0.8Si-0.2Cu alloys. Intergranular corrosion in the 0.1%Zn-containing alloy did not occur after baking treatment at 443K for 20 minutes. Figure 4 shows the effect of Zn content and heat treatment on the pitting potential of the Al-0.8Mg-0.8Si-0.2Cu alloy. The pitting potential of a solution-treated alloy decreased by the addition of Zn. The dissolution potential of the 0.1%Zn-containing alloy was the same as that of  $Mg_2Si$ . Therefore, as a result of no difference in the potential between the two, selective dissolution was suppressed. But in the alloys containing more than 0.1%, intergranular corrosion occurred. It was postulated that the intergranular corrosion mechanism was different from the preferential dissolution of  $Mg_2Si$  precipitates, because the dissolution potential of the alloys were lower than that of  $Mg_2Si$ . Figure 5 shows a SEM micrograph of the grain boundary after anodic dissolution for 1 hour. Morphology of the intergranular corrosion of Zn containing alloys suggested a solute depleted zone type. Figure 6 showed the mechanism of the Zn added alloys[3]. In Al-Mg-Si-Cu-Zn alloys, the Si-depleted zone was the least noble. Zn content in the alloys was considered to have an effect on the potential of the solute depleted zone.

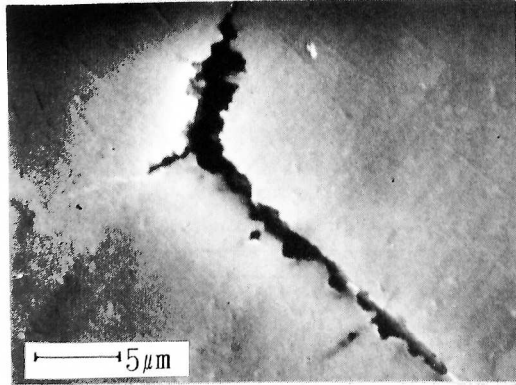


Figure 5 Surface observation of Zn-containing alloy after anodic dissolution for 1 hour.

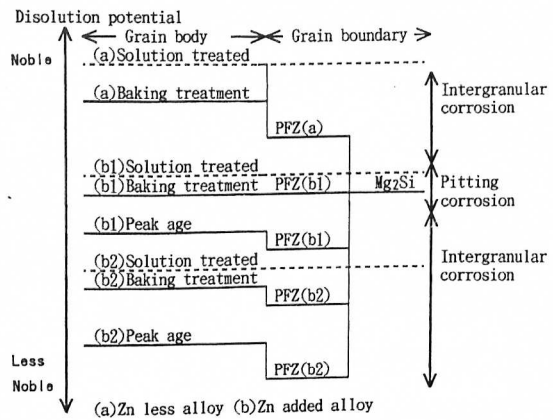


Figure 6 Schematic representation of intergranular corrosion mechanism of Al-Mg-Si-Cu-Zn alloys.

### 3.3 Effect of the corrosion characteristics on corrosion resistance of painted Al-Mg-Si series alloy sheet.

Figure 7 shows the effect of the Cu content in the alloys on the amount of the zinc phosphate film and on the length of the filiform corrosion. Although the phosphate film amount significantly increased with an increase in Cu content, the corrosion resistance deteriorated. Therefore, the corrosion characteristics had an important effect on the growth of the filiform corrosion. A cross-sectional view of filiform corrosion area is shown in Figure 8. The corrosion products under the painted film lifted the film, and severe intergranular corrosion of the aluminum alloy substrate was observed. In addition, the progress of intergranular corrosion under the adhered paint (a) and collapse of the grain (b) were also observed. As mentioned above, Zn addition had the effect of preventing intergranular corrosion of that described. Figure 9 shows the relationship between the amount of phosphate film and the length of the filiform corrosion[4]. The intergranular corrosion preventing 0.10%Zn-containing alloy had excellent corrosion resistance.

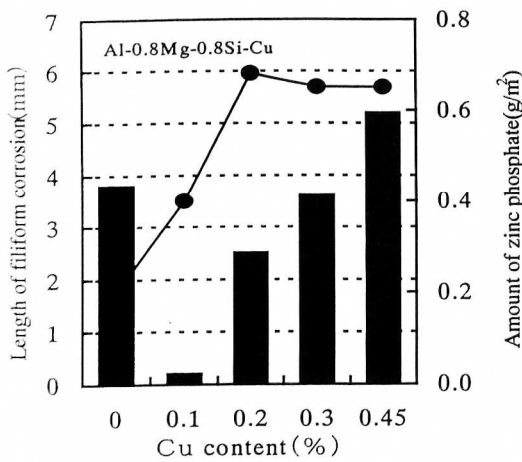


Figure 7 Effect of Cu content on amount of zinc phosphate film and length of filiform corrosion of Al-Mg-Si-Cu alloys.

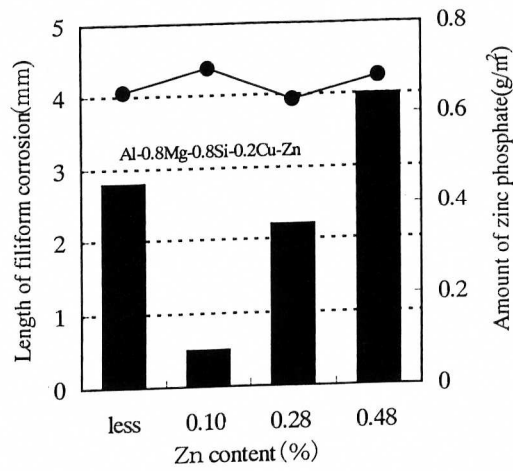


Figure 9 Relationship between the amount of phosphate film and the length of filiform corrosion of Al-Mg-Si-Cu-Zn alloys.

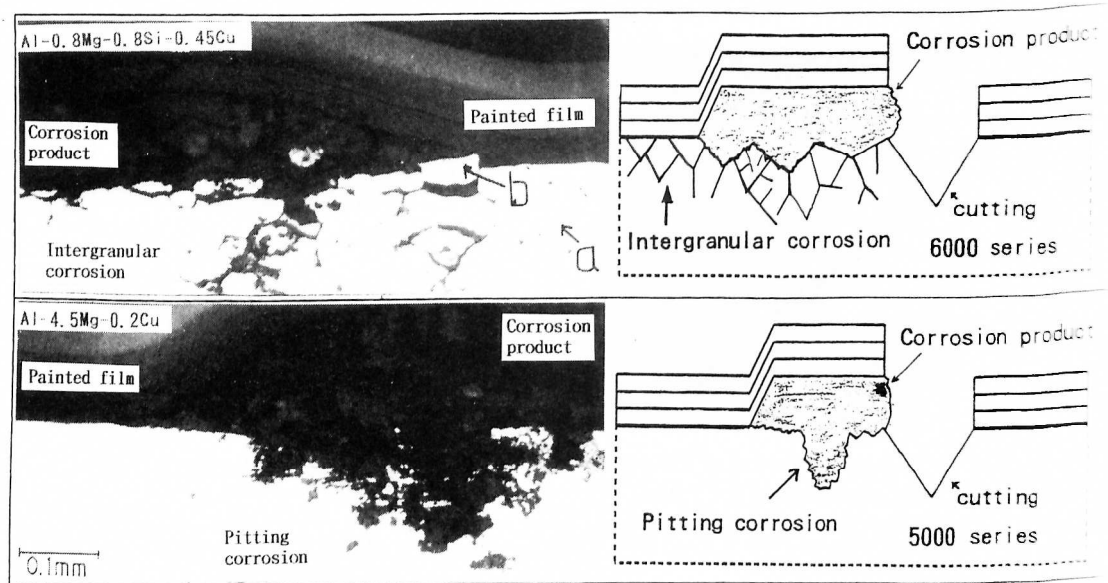


Figure 8 Cross-sectional view of corrosion area.

#### 4. CONCLUSIONS

The obtained results are summarized as follows.

- (1) Intergranular corrosion had an activated effect on the filiform corrosion growth under the paint film.
- (2) The alloys containing more than 0.2%Cu were susceptible to intergranular corrosion after the baking treatment. Intergranular corrosion occurred by the preferential dissolution of less noble  $Mg_2Si$  precipitates in the grain boundaries.
- (3) As a result of the difference in the potential between the two, it was reduced to almost zero by addition of the appropriate Zn, and intergranular corrosion was suppressed. Zn addition was effective to suppress the intergranular corrosion of Al-Mg-Si-Cu alloys.
- (4) Controlling the intergranular corrosion had a significant effect on improving the corrosion resistance of painted sheets.

#### REFERENCES

- [1] K. Yamaguchi and K. Tohma: J. Jpn. Inst. Light Metal, 47(1997), 285.
- [2] H. K. Farmery, J. Inst. Metals 84(1995~56), 413.
- [3] K. Yamaguchi and K. Tohma: 92th Conf. Jpn. Inst. Light Metal, (1997), 329.
- [4] K. Yamaguchi and K. Tohma: 93th Conf. Jpn. Inst. Light Metal, (1997), 63.