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# THE EFFECTS OF GRAINBOUNDARY PRECIPITATIONS ON THE STRESS CORROSION CRACKING OF AL-4～4.5MASS%MG ALLOYS

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**ABSTRACT** In order to improve stress corrosion cracking (SCC) resistance of Al-4.0～4.5mass%Mg alloys, the effects of Zn addition and stabilization condition on the SCC were investigated. Evaluations were conducted by changing Zn addition (0.5 and 1.0mass%), stabilizing temperature (240～320℃) and cooling method after stabilization (furnace cool and air cool). To increase the susceptibility to SCC, sheets were cold rolled with 30% reduction and sensitized at 100℃ for one year before SCC tests. The results were as follows: (1) Combination of 1mass%Zn addition and stabilization at 280℃ with furnace cool showed the most excellent SCC resistance. (2) A close correlation was found between the area fraction of grainboundary precipitates generated during stabilization and SCC resistance. (3) Zn addition with stabilization followed by furnace cool depleted Mg and Zn concentrations near grainboundaries, which changed the morphology of grainboundary precipitates during sensitization from film-like to particle.

**Keywords:** *Aluminium-Magnesium alloy, stress corrosion cracking, precipitates, Zn addition, stabilization, concentration profile, sensitization*

## 1. INTRODUCTION

Owing to high strength and good formability, Al-Mg alloy has great potential for structural applications such as automotive unibody, wheel and marine parts. Although lower Mg alloys, e.g. AA5052 are ubiquitous for structural applications[1], higher Mg alloys still have a lot of room to grow in the field where the necessity of weight reduction arises. The biggest problem which prevents high Mg alloys from actual use is their susceptibility to SCC. As Dix pointed out that Al-Mg alloys were liable to SCC when Mg content exceeded 3.5mass% due to the film form precipitation of $\beta$ phase along grain boundaries[2]. So, it is very important to develop higher Mg content(over 3.5mass%Mg) alloys with excellent SCC resistance in order to satisfy the demands for structural applications.

Recently, a suitable stabilization treatment was found to be effective to improve SCC resistance for Al-Mg alloys when Mg content was higher than 6mass%[3]. In case of Mg less than 6mass% alloys, however, the effect of the stabilization treatment was not enough to disregard SCC problem. On the other hand, Yukawa et al[4], P.Brenner and G.J.Metcalfe[5] reported that Zn addition could promote the precipitation of $\beta$ phase in Al-Mg alloys. The combination of stabilization treatment and promotion of precipitation with Zn addition can be useful for improving SCC resistance of Al-Mg alloys.

In this study, SCC resistance of Al-4,4.5mass%Mg-0,0.5,1.0mass%Zn alloys were evaluated using four points bending tests. The correlation between SCC resistance and the area fraction of grainboundary precipitates was investigated.

## 2. EXPERIMENTAL PROCEDURES

### 2.1 Preparation of materials

The chemical composition of alloys used in this study are listed in Table 1. The Al-Mg (4~4.5mass%)-Zn (0~1.0mass%) alloys were cast, hot rolled and cold rolled to 1mm thick sheets after homogenization and scalping. The sheets were annealed at 520°C for 15s followed by water quench. In order to control the morphology of precipitates, the sheets were stabilized at 240, 280, 320°C for 2hours, then air cooled (AC) or furnace cooled(FC) to room temperature.

Table 1 Chemical composition of alloys(mass%)

| Name of alloys | Mg | Zn | Fe | Si | Cr |
|---|---|---|---|---|---|
| Al-4mass%Mg | 3.94 | -- | 0.08 | 0.09 | -- |
| Al-4mass%Mg-0.5mass%Zn | 4.07 | 0.51 | 0.09 | 0.08 | -- |
| Al-4mass%Mg-1.0mass%Zn | 3.95 | 1.00 | 0.09 | 0.08 | -- |
| Al-4.5mass%Mg-1.0mass%Zn | 4.30 | 0.98 | 0.27 | 0.09 | 0.18 |

### 2.2 The method to evaluate stress corrosion cracking resistance

In order to increase the susceptibility to SCC, the sheets were cold rolled with 30% reduction and sensitized at 100°C for 1 year by following Dix's evaluation method[2]. The test pieces were cut from the sensitized sheets along the transverse direction and stressed to 80 percent of the 0.2% yield strength with a four points bent device, then immersed into 3.5%NaCl solution(35°C,pH;3.0). The solution was changed every two weeks. The time to failure was measured as SCC resistance. Three test pieces were evaluated for each alloy.

### 2.3 Microstructures

The stabilized sheets and sensitized sheets were polished and etched in 1% NaOH solution (40°C) for 1min. to outline precipitates. The precipitates were observed with optical microscopy in detail. The area fraction of precipitates were measured with an image analyzer(LUZEX F, made by Nileco Co.). Thin foils of some alloys used for TEM observation were prepared by twin-jet electro-polishing in a nitric-methanol solution at 253K. The precipitates were observed by H800 TEM. Microanalysis of Mg and Zn concentrations near grain boundaries were conducted with HF2000 TEM equipped with EDX. The electron beam diameter used for the analysis was about 20nm.

## 3. EXPERIMENTAL RESULTS

### 3.1 Effects of Zn content and stabilization on the susceptibility to SCC

Fig.1 shows the results of SCC tests on all prepared Al-Mg-Zn alloys in this study. Almost all the alloys broke in short time. However, Al-4,4.5mass%Mg-1.0mass%Zn alloys stabilized at 280°C for 2 hours followed by furnace cool didn't fail after 2 months(1440hours).

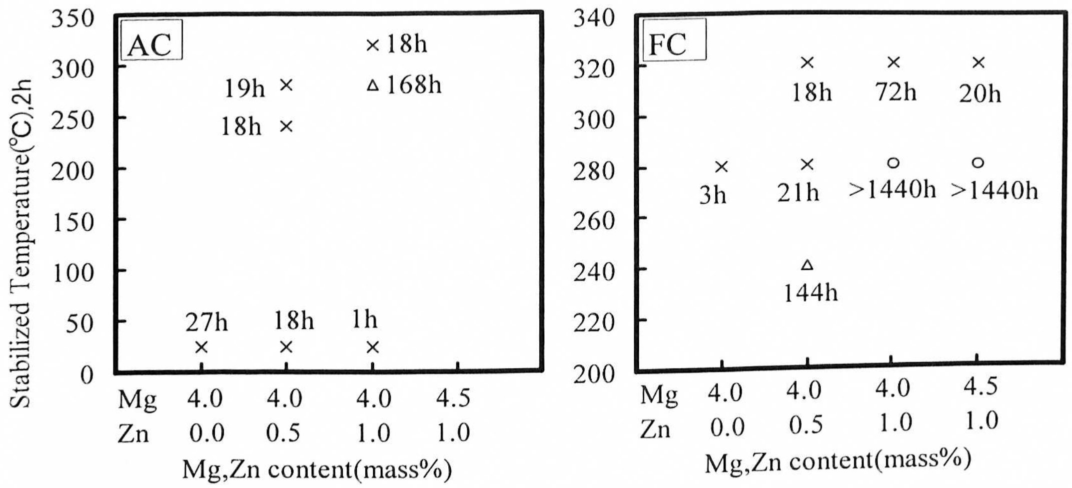


Fig.1 The results of SCC tests, the numeral in the figure representing the time to failure.

The correlation between SCC resistance and Zn content or stabilization conditions is shown in Fig.2. Without stabilization, time to failure became shorter as Zn content increased. However, with stabilization at 280℃, especially followed by furnace cool (280℃ FC), SCC became less susceptible as Zn content increased.

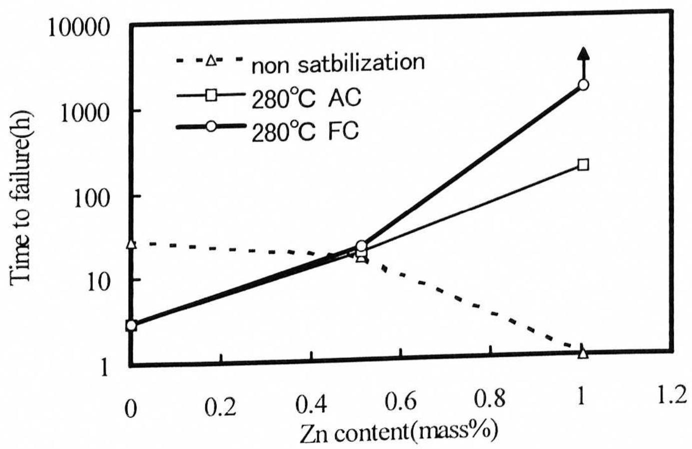


Fig.2 Effect of Zn content and stabilization on the susceptibility to SCC of Al-4mass%Mg based alloys.

### 3.2 Precipitates in stabilized alloys

Fig.3 shows microstructures of stabilized Al-4mass%Mg based alloys. Precipitates didn't exist in the 0mass%Zn alloy(a). Precipitates were observed in Al-4mass%-1mass%Zn alloy(b,c). The precipitates in the furnace cool(b) were larger and denser than those in the air cool(c). TEM micrograph of Al-4mass%Mg-1mass%Zn alloy stabilized at 280℃ followed by furnace cool is shown in Fig.3(d). The precipitates were identified as $\beta$ phase(Al-Mg) or $\tau$ phase(Al-Mg-Zn) by EDX and XRD with reference to Al-Mg-Zn ternary phase diagram[6].

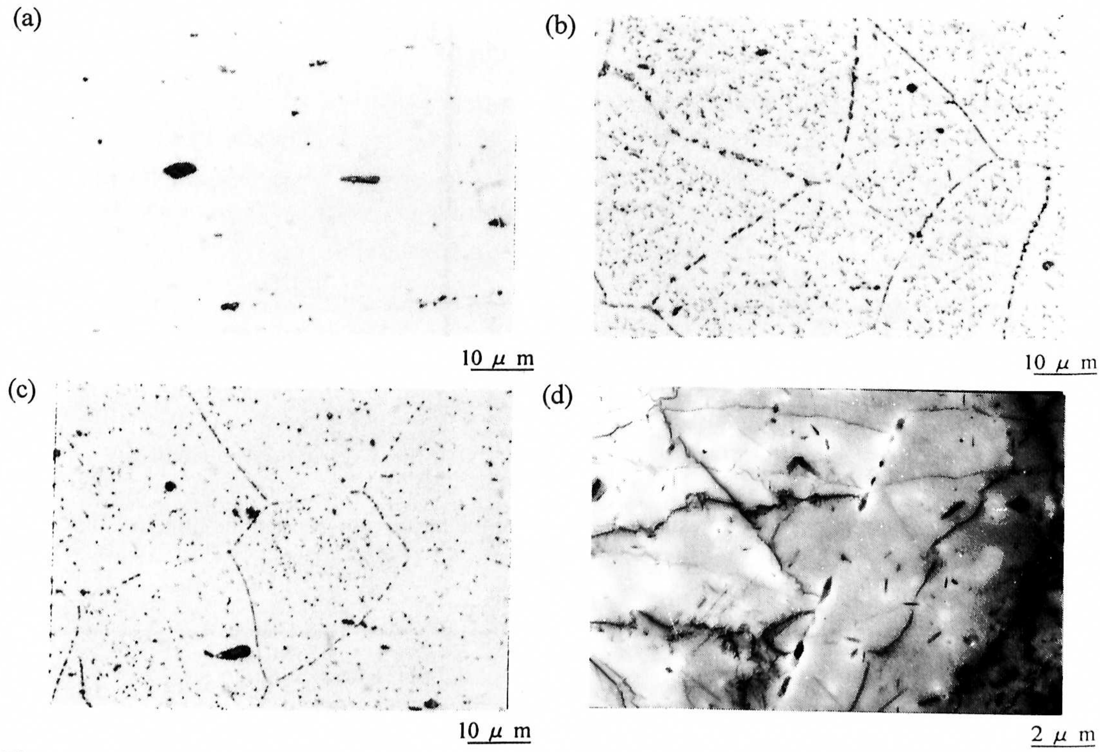


Fig.3 Optical micrographs (a~c) and TEM micrograph (d) of several Al-4mass%Mg based alloys. (a) Al-4mass% alloy, (b,d) Al-4mass%Mg-1mass%Zn alloy stabilized at 280°C for 2hours followed by furnace cool. (c)Al-4mass%Mg-1mass%Zn alloy stabilized at 280°C for 2hours followed by air cool.

**3.3 Precipitates in sensitized Al-Mg alloys**

Fig. 4 shows microstructures of Al-4mass%Mg based alloys sensitized at 100°C for 1 year. In Al-4mass%Mg alloy, $\beta$ phase seemed to be precipitated in the form of film(a). That is why Al-4mass%Mg alloy was very susceptible to SCC. However, the shape of precipitates in Al-4mass%Mg-1mass%Zn alloy with stabilization was different(b~d). Precipitates along grainboundaries in Al-4mass%Mg-1mass%Zn alloy stabilized at 280°C followed by furnace cool were not continuous(b). For this reason, their susceptibility to SCC became less. In Al-4mass%Mg-1mass%Zn alloy stabilized at 280°C followed by air cool, particles(c) or film-like precipitates(d) were observed. So, the susceptibility to SCC of Al-4mass%Mg-1mass%Zn alloy with air cool was less than that of Al-4mass%Mg alloy, but higher than that of Al-4mass%Mg-1mass%Zn alloy with furnace cool.

Actually, when Zn increased in Al-4mass%Mg based alloy without stabilization, $\beta$ phase(Al-Mg) or $\tau$ phase(Al-Mg-Zn) precipitated in the form of film along grainboundary distinctly during sensitization. So, SCC occurred within short time in Al-4mass%Mg-1mass%Zn without stabilization.

Therefore, the susceptibility to SCC could be explained by the difference of morphology of precipitates during sensitization. The alloy with precipitates in the form of film was very susceptible to SCC, the susceptibility to SCC became less as precipitates existed in the form of particle, which is in agreement with Dix's results[2].

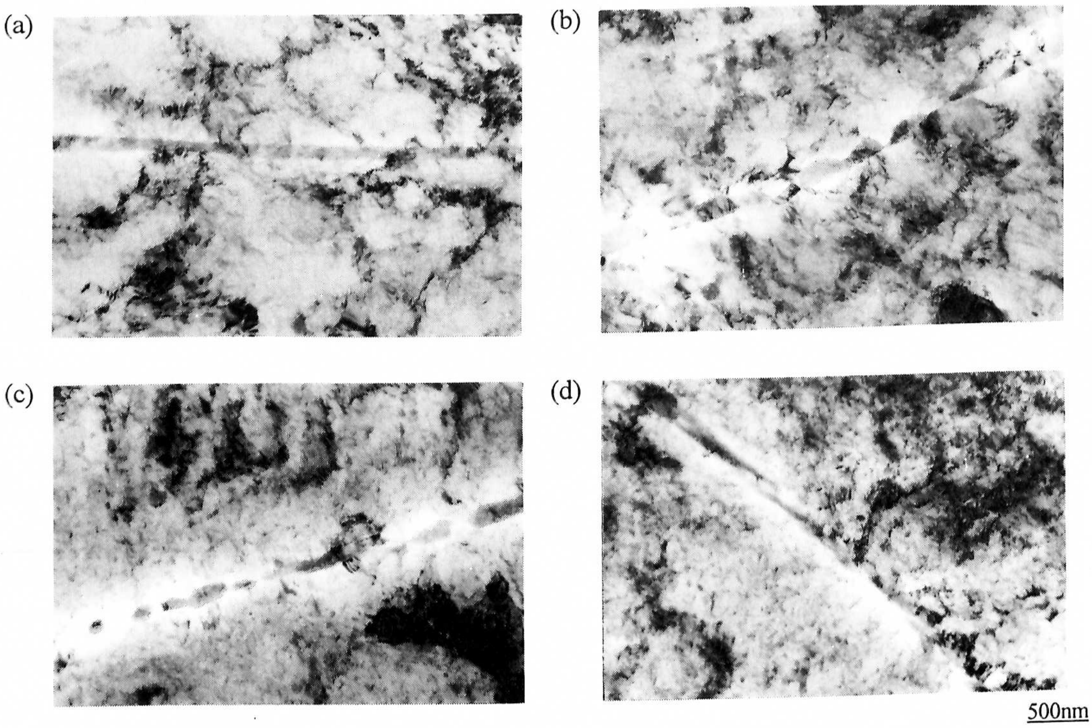


Fig.4 TEM micrographs of several Al-4mass%Mg based alloys sensitized at 100°C for 1year. (a) Al-4mass%Mg alloy, (b) Al-4mass%Mg-1mass%Zn alloy stabilized at 280°C for 2hours followed by furnace cool. (c,d) Al-4mass%Mg-1mass%Zn alloy stabilized at 280°C for 2hours followed by air cool.

## 4. DISCUSSION

Al-4mass%Mg-1mass%Zn alloy with a suitable stabilization became more difficult to precipitate along grainboundaries than Al-4mass%Mg alloy during sensitization. These phenomena can be explained by Mg and Zn concentration distribution near grainboundaries.

Fig.5 shows the profiles of Mg and Zn concentrations near a grainboundary measured by EDX. It is clear that the addition of 1mass%Zn and stabilization at 280°C followed by furnace cool (FC) lowered Mg and Zn concentrations markedly near grainboundaries. The gradient of concentration profile can be understood by the precipitation of $\beta$ phase(Al-Mg) or $\tau$ phase(Al-Mg-Zn) which absorbed Mg and Zn solutes in the matrix. Similar phenomenon was reported by Yukawa et al[4] on Al-9mol%Mg alloy. These results suggested that the precipitation of $\beta$ or $\tau$ phase during stabilization can delay the precipitation during sensitization and thus the resistance to SCC improved. The correlation between time to failure of sensitized Al-4,4.5mass%Mg-0,0.5,1mass%Zn alloys and area fraction of grainboundary precipitates generated during stabilization is shown in Fig.6. The higher the area fraction of precipitates is, the longer the time to failure becomes.

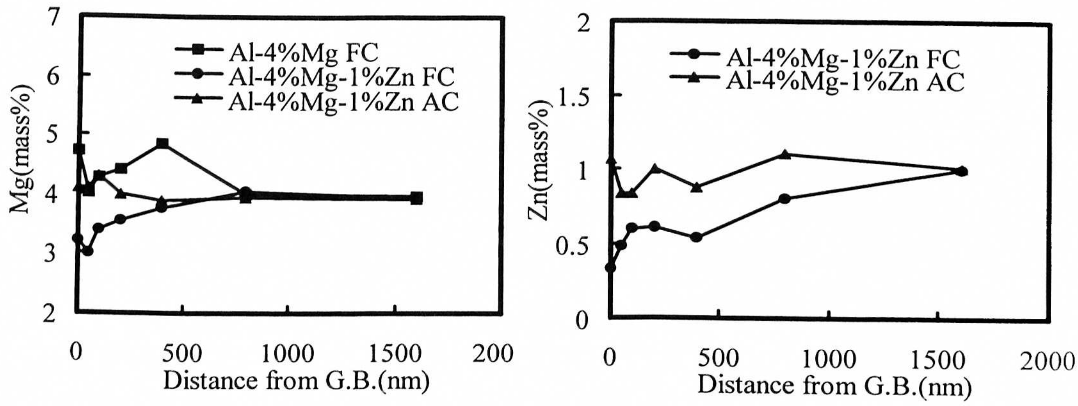


Fig.5 The profiels of Mg and Zn concentrations measured by EDX.

## 5. CONCLUSION

(1) The combination of Zn addition and proper stabilization treatment improved SCC resistance of Al-Mg alloys remarkably.

(2) A close correlation was found between the area fraction of grainboundary precipitates generated during stabilization and SCC resistance of sensitized Al-Mg based alloys.

(3) Zn addition with stabilization treatment followed by furnace cool depleted Mg and Zn concentrations near grainboundaries, which changed the morphology of grainboundary precipitates during sensitization from film-like to particle.

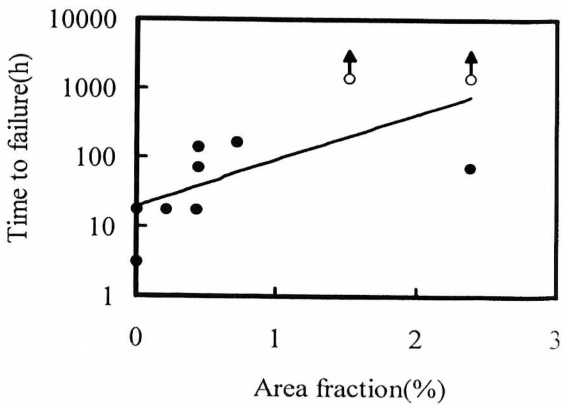


Fig.6 The correlation between amount of grain boundary precipitates and SCC resistance.

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