Stress Corrosion Cracking and Corrosion Resistance of Mg–6%Al–1%Zn–2%Ca Extruded Magnesium Alloys*1

Motohiro Yuasa¹*,2, Eitaro Yukutake², Xinsheng Huang¹, Kazutaka Suzuki¹,*3, Naobumi Saito¹ and Yasumasa Chino¹

¹Structural Materials Research Institute, National Institute of Advanced Industrial Science and Technology, Nagoya 463–8560, Japan
²Industrial Technology Institute of Ibaraki Prefecture, Higashibaraki-gun, Ibaraki 311–3195, Japan

Stress corrosion cracking (SCC) and corrosion resistance of Mg–6 mass%Al–1 mass%Zn–2 mass%Ca (AZX612) extruded alloy were investigated by slow strain rate tensile tests (SSRT) in 0.01 M NaCl solution and immersion tests in 5 mass% NaCl solution, and compared with those of Mg–6 mass%Al–1 mass%Zn (AZ61) extruded alloy. In the SSRT in the salt solution, as-received AZX612 exhibited lower elongation and higher SCC susceptibility than those of as-received AZ61, indicating that calcium addition in Mg–Al alloy deteriorated SCC resistance. On the other hand, after solution treatment, improvement of elongation and SCC susceptibility occurred in both the alloys. Observation of surface profiles for AZX612 and AZ61 after the SSRT in salt solution revealed that corrosion pits on surface likely initiated SCC in both the alloys. The results of immersion tests showed the same tendency with those of SSRT in salt solution. It is suggested that SCC resistance of AZX612 and AZ61 was likely related to the microstructural change accompanied with calcium addition and solution treatment such as the change in distributions of Al2Ca phase and Al-rich phase. [doi:10.2320/matertrans.L-M2017824]

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1. Introduction

Magnesium alloys constitute the lightest alloys among structural metals, and they are employed as light structural materials for automobiles. Some cast Mg alloys have recently been utilized in the automobile industry¹⁵. On the other hand, the low ignition properties of these alloys result in safety issues, especially in train and aerospace applications, because heating up to the melting temperature in air atmosphere increases the risk of ignition and combustion. Thus, the application of Mg alloys in these areas is highly restricted. Recently, a “flame retardant Mg alloy” with excellent flame retardant properties has been developed, and extensive research has been pursued for the utilization of these alloys in train and aerospace²⁴. Currently, its small products are used to construct components of trains³¹. To drastically reduce the weight of train and aircraft bodies using flame retardant Mg alloys, it is essential to energetically develop process technologies for large wrought alloy products and evaluation methods for the certification of reliability (such as fatigue and corrosion properties). In particular, for outdoor applications, systematic testing of the stress corrosion cracking (SCC) properties under various environmental conditions is necessary.

It has been reported that SCC in Mg alloys is strongly influenced by their composition and microstructure³¹. For example, Faiman³⁰ reported that the SCC susceptibility increases with an increase in the Al content of Mg alloys. Kannan et al.³² investigated the SCC resistance of Mg alloys with rare-earth additives and reported that the SCC resistance varies significantly with the alloy composition. The reason for this is ascribed to variations in the intermetallic phases depending on the alloy composition (as a result, there is a difference in electrode potential between the matrix and the intermetallic phases.) Argade et al.³⁰ reported that the SCC susceptibility increases concomitantly grain refinement, where the reason is explained to be connected to differences in intragranular and transgranular diffusion rates of hydrogen.

Although there are many reports concerning the SCC of Mg alloys, discussion on the relationship between composition and microstructure is still in progress. Besides, to the best of our knowledge, there has been no research on the SCC of flame retardant Mg alloys (Mg-Al-Ca series alloys). In this study, the relationship between SCC and corrosion resistance under salt water corrosion environments has been investigated, for the purpose of clarifying the SCC phenomenon in extruded flame retardant Mg alloys. In particular, the SCC and corrosion resistance of the alloys in the extruded Mg-Al-Ca series and Mg-Al series before and after solution treatment were investigated. In addition, the effects of microstructural changes accompanying Ca addition and solution treatment on the SCC and corrosion resistance of the alloys were evaluated.

2. Experimental Procedure

In this study, AZX612 and AZ61 as representatives of Mg-Al-Ca and Mg-Al alloy extrusions, respectively, were chosen. The extrusions, with a thickness of 3 mm, were provided by Sankyo Tateyama, Inc.. The compositions of the as-received materials are shown in Table 1. The concentrations of impurities such as iron, copper, and nickel, which deteriorate corrosion resistance³⁰, were almost the same in AZX612 and AZ61. To investigate the effects of intermetallic phases and solute segregation in the matrix on the SCC and corrosion resistance, the properties of the as-received and solution-treated (processed by solution treatment at
420°C for 48 h) materials were evaluated.

Slow strain rate tensile tests (SSRT) under a saltwater corrosion environment were carried out in order to evaluate the SCC resistance of the abovementioned materials. Specimens 5 mm in width and 30 mm in length of the parallel part were machined from the extrusions, and the tensile direction was set parallel to the extrusion direction. The surface of the machined specimens was dry-polished using SiC paper (grid number #220 to #2400) and degreased by ultrasonic cleaning in ethanol for 5 min. 0.01 M (0.59 mass%) NaCl solution, whose pH was adjusted to 10 by Mg(OH)₂, was used as the test solution. A constant strain rate tensile testing machine (TOSHIN KOGYO Co., LTD. SERMINI-10T) was used. Tensile tests were carried out at an initial strain rate of 10⁻⁶ s⁻¹, where the parallel part of the tensile specimen was immersed in the test solution adjusted to 35°C. The solution volume to specimen area ratio, when the specimen was immersed in the test solution, was set to more than 80 mL/cm². For reference, tensile tests were carried out at room temperature (air atmosphere; initial strain rate: 10⁻⁶ s⁻¹).

The index of SCC susceptibility (I_SCC) was calculated in order to evaluate the SCC resistance, where in air atmosphere and in salt water was defined as in inert environment and in corrosion environment, respectively. I_SCC was calculated from eq. (1) by using the failure elongation in each environment (ε_f_air, ε_f_SCC)\(^3\),\(^10\).

\[
I_{SCC} = \frac{\varepsilon_{f,air} - \varepsilon_{f,SCC}}{\varepsilon_{f,air}}
\]  

After the SSRT, the corrosion product on the specimens was removed using a boiling chromic acid solution containing 10 mass% CrO₃, and then, the surface appearance near the fractured part of the specimen was observed by scanning electron microscopy (SEM). For observing the pitting corrosion and crack propagation simultaneously, the specimens were cut so that the ED-ND plane could be observed. After the ED-ND plane was polished to a mirror surface, observations were carried out at a slant angle of 45° from the ED-TD and ED-ND planes, so that both the ED-TD and ED-ND planes could be simultaneously observed; here, the ED-TD plane was immersed in salt water.

In order to evaluate the corrosion properties of the specimens, salt water immersion tests based on JIS H0541 were carried out. Specimens with dimensions of 25 mm x 35 mm x 3 mm were machined from the as-received and solution-treated samples and wet-polished using SiC paper (grid number #220 to #1000). The specimens were immersed in the test solution, i.e., 5 mass% NaCl solution, at 35°C for 72 h, where pH was adjusted to 10 by Mg(OH)₂. After the immersion tests, the corrosion product was removed using boiling chromic acid solution containing 10 mass% CrO₃. Then, the weight loss of the specimen was measured to determine the corrosion rate, using the following equation: \( R = 8.76 \times 10^4 \times \frac{W}{(T \times A \times D)} \), where W: weight loss of specimen (g), T: testing time (h), A: surface area of specimen (cm²), and D: density of specimen (g cm⁻³). For investigating the surface state of the specimens after the salt immersion tests, the surface depth profile of the specimens was measured by using a surface roughness tester (SURFTEST SJ-500, Mitutoyo).

3. Results and Discussion

3.1 Microstructures of AZX612 and AZ61 extrusions

Optical micrographs of the AZX612 and AZ61 extrusions are shown in Fig. 1. Both the as-received and solution-treated AZX612 exhibited a duplex grain structure. The grain size of the coarse and fine grain parts was 158 µm and 8 µm, respectively, for the as-received specimen; the corresponding values for the solution-treated specimen were 160 µm and 10 µm. Variations in the grain size due to solution treatment appeared to be small, at least in the optical microscope observations. On the other hand, the microstructure of the as-received AZ61 was composed of equiaxial grains having sizes of 37 µm, and abnormal grain growth was observed in the solution-treated AZ61. The grain size was 42 µm except in the region where abnormal grain growth was observed. Numerous intermetallic phases were observed in AZX612, as opposed to AZ61, and the intermetallic phases were distributed parallel to the extrusion direction.

SEM observations were carried out for precise understanding of the alignment and distribution of the intermetallic phases. The results are shown in Fig. 2. In the as-received AZX612, relatively fine intermetallic phases with diameters of about 1–2 µm, and relatively large intermetallic phases with diameters of about 5 µm were distributed parallel to the extrusion direction. The intermetallic phases in the solution-treated AZX612 exhibited non-dense distribution than those in the as-received AZX612. In the case of AZ61, relatively large intermetallic phases with diameters of about 5 µm were distributed parallel to the extrusion direction,

| Table 1 Chemical composition of the as-received extruded AZX612 and AZ61. |
|---|---|---|---|---|---|---|---|
|   | Al | Zn | Mn | Ca | Fe | Cu | Ni | Mg |
| AZX612 | 5.9 | 0.5 | 0.27 | 2.0 | 0.002 | <0.002 | <0.002 | Bal |
| AZ61 | 5.9 | 0.6 | 0.28 | <0.002 | 0.002 | <0.002 | <0.002 | Bal |

Fig. 1 Optical micrographs of the (a) as-received AZX612, (b) solution-treated AZX612, (c) as-received AZ61 and (d) solution-treated AZ61. The white arrows indicate the intermetallic phases distributed along the extruded direction.
while the total amount of intermetallic phases in AZ61 was smaller than that in AZX612. The size and distribution of the intermetallic phases in AZ61 were almost the same between the as-received and solution-treated specimens.

XRD analysis was carried out to identify the type of intermetallic phases observed in Fig. 2. The results are summarized in Fig. 3. Peaks due to the Al2Ca and Al-Mn series compounds, in addition to those due to the α-Mg matrix, were observed in the XRD spectrum of AZX612. There was no distinct difference in the peaks between the as-received and solution-treated specimens. Peaks attributed to the Mg17Al12 phase (β phase), which was observed in the Mg-Al series alloys with high Al concentrations, were not clearly identified11). The possible reason for the insignificant change in the grain size of AZX612 before and after solution treatment in Fig. 1 is that the finely and homogeneously distributed Al2Ca phases suppressed grain growth. Terada et al.12) investigated the microstructures of die-cast products made of Mg-Al-Ca series alloys before and after solution treatment, and reported that a part of the Al2Ca phase is dissolved in the matrix after solution treatment. This was possibly because Mg atoms existing as substitution-type solid solution elements in the Al2Ca phase dissolved in the matrix. The conditions adopted for the solution treatment in our study are similar to those reported by Terada et al. Thus, it can be considered that the Al2Ca phase distributed in the AZX612 specimen used in the present experiment also partly dissolved in the matrix. As a result, the solution-treated specimens exhibited non-dense distribution of Al2Ca phase compared with the as-received specimens. In the case of AZ61, peaks due to the α-Mg matrix and Al-Mn series compounds were identified in both the as-received and solution-treated specimens. No distinct change in the peaks due to solution treatment was observed, as in the case of AZX612.

3.2 Stress corrosion cracking properties of AZX612 and AZ61 extrusions

Stress-strain curves obtained by the SSRT in air and salt water are shown in Fig. 4. The ultimate tensile strength (UTS), failure elongation, and SCC susceptibility are summarized in Table 2.

The results obtained in the air environment indicated that AZX612 exhibited increased elongation upon solution treatment. This is possibly because the number of crack initiation
sites decreased with solution treatment because of dissolution of a part of the Al$_2$Ca phase in matrix. On the other hand, the AZ61 exhibited decreased elongation after solution treatment, likely because of the significant grain coarsening$^{[13]}$. It should be noted that a decrease in UTS accompanied with solution treatment was observed especially in the AZX612.

Next, the results obtained in the salt water environment revealed that the as-received AZX612 and AZ61 showed a lower UTS and failure elongation as compared with those in air. In particular, the as-received AZX612 had lower elongation and higher SCC susceptibility than the as-received AZ61. Thus, it is clarified that Ca addition to the Mg-Al series alloys deteriorated their SCC resistance. Atrens et al.$^{[14]}$ investigated the effects of the $\beta$ phase in AZ91 (Mg–9 mass%Al–1 mass%Zn) on the SCC. They reported that hydrogen trapped around the $\beta$ phase deteriorates the toughness of the matrix, and that the introduction of hydrogen promotes large dislocation mobility, resulting in increased SCC. The results illustrated in Fig. 4 and Table 2 indicate that the existence of the Al$_2$Ca phase in AZX612 promoted an increase in the SCC susceptibility in the same manner as the $\beta$ phase in AZ91. On the other hand, the results for the solution-treated specimens indicated that the difference in failure elongation between the air and salt water environments decreased, resulting in a low index of SCC susceptibility. This trend was the same between AZX612 and AZ61, and the SCC resistance was confirmed to improve with solution treatment, regardless of Ca addition. Incidentally, for AZ61, there was no large change in the distribution and size of the intermetallic phases before and after solution treatment. It is presumed that different factors from the intermetallic phases also affected the SCC susceptibility.

Next, in order to investigate the effects of the test environment on the fracture morphologies of the specimens, the fracture surface (around fracture surface) after the SSRT was observed by SEM. The results for AZX612 and AZ61 under different environments are shown in Fig. 5 and Fig. 6, respectively.

In the case of the specimens that were tensile-deformed in air, smooth concavity and convexity ranging from several dozen micrometers to 100$\mu$m were observed on both the surface of both AZX612 and AZ61. Since the period of concavity and convexity was similar to the grain size, it can be presumed that the concavity and convexity corresponded to evidence for grain boundary sliding during the SSRT$^{[15]}$.

In the specimens tensile-deformed in salt water, corrosion pits distributed perpendicular to the tensile direction could be observed on the ED-TD plane, which was not the case for the specimens tensile-deformed in air. It was observed on the ED-ND plane that cracks arising from the corrosion pits propagated toward the interior of the matrix. The formation frequency and size of the corrosion pits and cracks observed on the specimen surface were almost the same, regardless of Ca addition and solution treatment. Larger corrosion pits and cracks were observed on the surface of the solution-treated AZX612 than on the as-received AZX612. This was because the failure strain of the solution-treated AZX612 deformed to failure was larger than that of the other specimens, and the specimens were submerged in solution for a long time. Winzer et al.$^{[16]}$ investigated SCC initiation of cast AZ91, extruded AZ31, and extruded AM30. They reported that in the case of cast AZ91, corrosion pits were not observed on the specimen surface, and the cracks formed at the $\beta$ phases became the sites of SCC initiation. In addition, they reported that in the case of the extruded AZ31 and AM30, the corrosion pits on specimen surface become the sites of SCC initiation. Thus, the fracture mode was reported

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Specimen</th>
<th>UTS (MPa)</th>
<th>$\varepsilon_\text{f}$ (%)</th>
<th>$I_{\text{SCC}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZX612</td>
<td>As-received</td>
<td>266.2 ± 6.3</td>
<td>16.9 ± 0.7</td>
<td>0.70</td>
</tr>
<tr>
<td>AZX612</td>
<td>Solution-treated</td>
<td>255.6 ± 4.7</td>
<td>19.3 ± 0.1</td>
<td>0.49</td>
</tr>
<tr>
<td>AZ61</td>
<td>As-received</td>
<td>287.0 ± 1.1</td>
<td>20.8 ± 1.8</td>
<td>0.58</td>
</tr>
<tr>
<td>AZ61</td>
<td>Solution-treated</td>
<td>283.8 ± 0.7</td>
<td>16.9 ± 0.2</td>
<td>0.38</td>
</tr>
</tbody>
</table>
to vary depending on differences in the Al concentration and microstructure. In the present experiments, since corrosion pits were observed on surface of all the specimens, it can be suggested that corrosion pits and cracks formed under the corrosion environments became initiated SCC, at least in the case of the extruded AZX612 and AZ61.

### 3.3 Relation between stress corrosion cracking and corrosion properties

As shown in Fig. 5 and Fig. 6, the corrosion pits and cracks on the surface of the extruded AZX612 and AZ61 caused SCC initiation. Next, the corrosion behaviors of the specimens without stress imposition were investigated by salt water immersion tests, and the effects of corrosion pits on the SCC behavior were evaluated by comparing the results of the salt water immersion tests and SSRT.

The corrosion rates calculated from the results of the salt water immersion tests are summarized in Fig. 7. As-received AZX612 exhibited a twofold higher corrosion rate than did AZ61, indicating that the corrosion properties deteriorated into Ca addition. On the other hand, the corrosion rates of the solution-treated AZX612 and AZ61 decreased and were almost identical to each other. This result qualitatively corresponded to that of the SSRT in salt water, where the index of SCC susceptibility for AZX612 and AZ61 decreased with solution treatment.

The surface appearances of the specimens after salt water immersion tests (appearance after removal of corrosion products) are shown in Fig. 8. In the case of the as-received AZX612, deep corrosion pits were continuously distributed in a part of the specimen. On the other hand, in the case of AZ61, corrosion pits shallower than those in AZX612 were observed over a wide region of the specimen. The results of the solution-treated specimens revealed few corrosion pits was on the surface of both AZX612 and AZ61.

Figure 9 shows the depth profiles around corrosion pits formed during the immersion tests, as measured using a sur-

![Fig. 6](image)

![Fig. 7](image)

![Fig. 8](image)
face roughness tester. In the depth profile measurements, the surface roughness of regions where relatively large corrosion pits were observed was measured. The as-received AZX612 exhibited deeper pits as compared to the as-received AZ61, and the formation frequency of the corrosion pits (initiation sites) decreased after solution treatment in both AZX612 and AZ61. The values of $R_a$ (arithmetic mean surface roughness) and $R_y$ (maximum depth) shown in Fig. 9 were closely related to the surface depth profiles.

Thus, the salt water immersion tests gave qualitatively the same results as the SSRT in salt water; the corrosion rate increased with Ca addition, the corrosion rate significantly decreased with solution treatment, etc. These results indicate that the formation behaviors of corrosion pits associated with corrosion advancement was an important factor dominating the SCC behavior. The above information may be act as evidence for the microstructural changes accompanying Ca addition and solution treatment that directly affected the SCC behaviors.

The microstructural factors for which the SCC resistance of AZX612 deteriorated into Ca addition are ascribed to the formation of the Al$_2$Ca phase after Ca addition. In addition, the microstructural factors for which the SCC resistance of AZX612 improved upon solution treatment are likely ascribed to a decrease in the number and size of the Al$_2$Ca phase due to dissolution in the matrix during solution treatment (Fig. 2 (a), (b)). In general, the intermetallic phases in Mg alloys have a more noble corrosion potential than the matrix, and the interface between the intermetallic phases and the matrix becomes the site of a local cell$^{17,18}$. Thus, it can be considered that the distribution of the Al$_2$Ca phase has a direct influence on the SCC behavior, because the interface of the Al$_2$Ca phase and the matrix may become the site of a local cell (corrosion pit).

It is suggested that an Al-concentrated matrix (Al-rich phase) around the intermetallic phases is another microstructural factor affecting the SCC behavior. Figure 10 shows a schematic diagram of the microstructure of the Mg alloy before and after solution treatment. Raman$^{19}$ investigated the corrosion properties of cast AZ91 and reported that corrosion preferentially occurs around the $\beta$ phase, when the Al-rich phase is distributed around the $\beta$ phase. In addition, Casajus et al.$^{20}$ pointed out that the area of the Al-rich phases decreases after heat treatment. Besides, our preceding study confirms the existence of an Al-rich phase in cast AZX612 and cast AZ61$^{21}$. Thus, it can be considered that the Al-rich phase around the $\beta$ phase likely decreased upon solution treatment, as shown in Fig. 10, and this decrease suppressed the formation of corrosion pits. In the case of AZ61, wherein there was no change in the distribution and size of intermetallic phases before and after solution treatment, it is suggested that the variation in the area of the Al-rich phase had a dominant influence on the SCC behavior.

In general, the discussion underlying the SCC mechanism in Mg alloys is often related to hydrogen absorption. Hydrogen embrittlement caused by hydrogen penetration from the specimen surface (newly formed surface) during deformation is suggested to be one of SCC mechanisms, which is applicable to the present experimental results (the results of SSRT in salt water)$^{22-24}$. For example, Stampella et al.$^{22}$
suggested that hydrogen generation occurs in association with the anode dissolution of Mg at the newly formed surface, which are newly formed accompanied with formation of corrosion pits. They also suggested that hydrogen penetration from the newly formed surface induces crack propagation (SCC). Thus, it cannot be denied that hydrogen penetration contributed to the formation of the cracks observed in Fig. 5 and Fig. 6. Unfortunately, hydrogen behavior was not investigated in the present experiments, and hence, it is impossible to discuss the relationship between variations in hydrogen behavior and the differences in composition and microstructure. The present experimental results indicate that variations in the generation of corrosion pits, which are associated with an increase or decrease in the concentration of intermetallic phases and Al-rich phase, are closely related to the SCC behavior. In the future, detailed investigations on the relationship between the abovementioned microstructural changes and hydrogen penetration are required.

4. Conclusions

For clarifying the SCC phenomenon of flame retardant Mg alloys under salt water corrosion environments, the SCC phenomenon and corrosion properties of extruded AZX612 and AZ61 were investigated and compared. The obtained results are as follows:

(1) In the SSRT in salt water, the as-received AZX612 exhibited lower failure elongation and higher index of SCC susceptibility than did the as-received AZ61. This result confirmed that Ca addition tended to deteriorate SCC resistance. On the other hand, the solution-treated AZX612 and AZ61 exhibited higher failure elongation in salt water and lower index of SCC susceptibility, as compared with the as-received AZX612 and AZ61. Observations of the specimen surface after SSRT in salt water indicated that many corrosion pits and cracks were formed on the specimen surface, and that the corrosion pits became initiation sites of SCC in AZX612 and AZ61.

(2) The results of salt immersion tests (corrosion rate) and SSRT in salt water (failure elongation and index of SCC susceptibility) exhibited qualitatively the same trend, and indicating a strong correlation between the tests. These results suggested that the formation behavior of the corrosion pits associated with corrosion advancement is a dominant factor affecting the SCC behavior, and that microstructural changes associated with Ca addition and solution treatment had a direct influence on the SCC behavior.

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REFERENCES