Microstructure and Corrosion Properties of Mg-xSn-5Al-1Zn (x = 0, 1, 5 and 9 mass%) Alloys

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In the present work, the corrosion properties of Mg-xSn-5Al-1Zn (x = 0, 1, 5 and 9 mass%) alloys have been investigated. Potentiodynamic polarization and immersion tests were carried out in 3.5% NaCl solution of pH 7.2 at room temperature to measure the corrosion properties of Mg-xSn-5Al-1Zn (x = 0, 1, 5, and 9 mass%) alloys. Microstructural analysis shows the Mg$_2$Al$_3$ and Mg$_2$Sn phase were mainly precipitated along grain boundaries. With increase of the Sn contents, the volume fraction of the secondary phases, i.e. Mg$_2$Al$_3$ and Mg$_2$Sn phase, was increased. The corrosion resistance of Mg-xSn-5Al-1Zn alloys was improved by the Sn addition. Especially, the AZ51-5 mass%Sn alloy characterized the superior corrosion resistance in the studied alloys. It seems that the presence of Sn stabilized the Mg(OH)$_2$ layers on the surface of Mg alloys and the secondary phases effectively formed semi-continuous structures, resulting in a drastic improvement of corrosion resistance of the Mg alloys.  [doi:10.2320/matertrans.M2009308]

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1. Introduction

Nowadays, magnesium alloys are being widely applied to structural parts, especially automotive and mobile electronic parts due to the lowest density in the structural materials, excellent mechanical properties, superior electric shielding and superior damping capacity.¹⁻¹³ Among the magnesium alloys, AZ91D, AZ31 and AM60 are the most widely used as commercial alloys, and they are applied to the automotive parts, i.e. cylinder head, steering wheel core, seat frame and so on. Although they are used widely in automotive industry, their applications are limited to the parts operated at temperature below 120°C because they show poor creep resistance and large decrease in strength at elevated temperature due to the thermal instability of microstructure. Moreover, magnesium is also well known as a very active metal and its alloys have a low corrosion resistance, resulting in restricted application of magnesium alloys to exposure environment. Therefore, in order to be extensively used in the automobile industry it is very important to improve the elevated temperature properties and corrosion resistance of magnesium alloys.

Many intensive and extensive fundamental investigations on the creep property and corrosion resistance of the magnesium alloys have been carried out during the past decade.⁵⁻¹³ The common way of improving heat-resistance of magnesium alloys is to form thermally stable precipitates to prevent grain boundary sliding during the creep deformation. On the other hand, the corrosion resistance of magnesium alloys was improved by forming a continuous secondary phases acting as a corrosion barrier or adding elements may incorporate into the protective film and thus increasing its stability. The most effective alloying elements for such purpose are rare earth metals which result in a significant improvement of creep and corrosion resistance. However, these elements are expensive, limiting widespread application of such alloys.

Recent studies indicated that the addition of Sn to Mg-Al binary system could contribute to strengthening magnesium alloys at elevated temperature because Mg$_2$Sn phase has high melting temperature of about 770°C.¹⁴⁻¹⁶ Furthermore, it is known that Sn is low cost material and has a high hydrogen overvoltage which can improve the corrosion resistance when it is used as a major alloying element. Besides the decision to apply Sn as a major alloying element, elements like Al, Zn, Ca, Si and Mn have been chosen as ternary alloying elements due to their influence on the formation of intermetallics to improve mechanical and corrosion properties.

In the present study, the effect of Sn additions on corrosion behavior of Mg-xSn-Al-Zn alloy was investigated on the basis of immersion and potentiodynamic test in 3.5% NaCl solution of pH 7.2 at ambient temperature.

2. Experimental

2.1 Materials

All materials investigated in the present study are listed in Table 1. The alloys were fabricated by squeeze casting in a mild steel crucible under a CO$_2$+SF$_6$ protective gas atmosphere. Starting materials were commercial alloys of Mg (99.9%), Sn (98.9%), Al (98.9%) and Zn (99.9%). Melting was carried out in an electric resistant furnace at 750°C and cast into a preheated (350°C) permanent steel mold with a dimension of 4 cm in thickness, 5 cm in width, and 10 cm in height. The pressure of plunger was 50 MPa and was kept for 60 s.

<table>
<thead>
<tr>
<th>Metallurgy Designation</th>
<th>Alloys</th>
<th>Sn</th>
<th>Al</th>
<th>Zn</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ51</td>
<td>Mg-5Al-1Zn</td>
<td>—</td>
<td>5</td>
<td>1</td>
<td>Bal.</td>
</tr>
<tr>
<td>TAZ151</td>
<td>Mg-1Sn-5Al-1Zn</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td>Bal.</td>
</tr>
<tr>
<td>TAZ551</td>
<td>Mg-5Sn-5Al-1Zn</td>
<td>5</td>
<td>5</td>
<td>1</td>
<td>Bal.</td>
</tr>
<tr>
<td>TAZ951</td>
<td>Mg-9Sn-5Al-1Zn</td>
<td>9</td>
<td>5</td>
<td>1</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

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2.2 Microstructures

For the microstructure observations, the samples of all alloys listed in Table 1 were initially ground in emery papers and then finally polished with 0.25 µm diamond paste. The polished samples were etched with a 3% nital solution (97 mL ethanol and 3 mL nitric acid) for 3–5 sec. Microstructural analysis was carried out using a scanning electron microscope (SEM; Hitachi S-4300) equipped with an energy dispersive X-ray spectrometer (EDS). Volume fractions of intermetallics were measured by an image analyzer. And the phases were analyzed via X-ray diffraction (Rigaku, CN2301) using monochromatic CuKα radiation in as-cast state.

2.3 Corrosion properties

2.3.1 Potentiodynamic polarization test

Potentiodynamic polarization test was carried out to easily understand the effects of the Sn addition on the corrosion resistance of the Mg-5Al-1Zn alloy. The test was conducted in 3.5% NaCl solution of pH 7.2 at 25°C by using an Electrochemical Interface Solartron SI 1287. A platinum gauze (25 mm × 25 mm, 60 mesh) was used as a counter electrode, and an Ag/AgCl electrode (in saturated KCl) was used as a reference electrode. Polishing was carried out on samples with SiC paper up to 600 grits before starting measurements. The experiments were done at least three times and the solutions were neither deaerated nor stirred. During electrochemical corrosion tests, electrode potential was measured at a scan rate of 0.2 mV/s from −0.3 V versus open circuit potential (OCP) to −0.8 V versus reference.

2.3.2 Immersion test

For the immersion test, rectangular samples with a dimension of 25 × 12 × 10 mm were prepared. The specimens were cleaned with alcohol, acetone and distilled water. After cleaning, these samples were weighed and then immersed in 3.5% NaCl solution of pH 7.2 at 25°C for 24, 72 and 120 h. At the end of the experiment, cleaning of specimens was carried out by dipping in a solution of 20% CrO3 and 2%AgNO3 in 100 mL distilled water at boiling condition. The weight loss was measured after each experiment and the corrosion rate was calculated in mg/cm²/day. The specimens were weighed on an analytical balance to an accuracy of ±0.1 mg.

3. Results and Discussion

3.1 Microstructure

The X-ray diffraction patterns of these alloys used in this study are shown in Fig. 1. The AZ51 alloy was mainly composed of \(\alpha\)-Mg and Mg\(_{17}\)Al\(_{12}\) phase, while the alloys with Sn addition consisted of three phases, i.e., \(\alpha\)-Mg, Mg\(_{17}\)Al\(_{12}\) and Mg\(_{2}\)Sn. On the other hand, neither the Al-Sn intermetallic nor the ternary phase was detected. The electro-negative values of Mg, Al, Zn and Sn are 1.31, 1.61, 1.65 and 1.96, respectively.\(^{17}\) Since the difference between Mg and Sn is the largest among the binary systems, the Mg–Sn compound was preferred to be formed in the Mg–Sn–Al–Zn system. It is consistent with the Mg–Zn–Al, Mg–Zn–Sn and Mg–Al–Sn ternary equilibrium phase diagrams.

![Figure 1](image.png)  
**Fig. 1** X-ray diffraction patterns of AZ51 alloys with and without Sn addition.

Figure 2 shows SEM micrographs and EDS spectrum of secondary phase in as-cast AZ51 alloys with different Sn contents. In AZ51 alloy, the Mg\(_{17}\)Al\(_{12}\) phase was observed along grain boundaries (Fig. 2(a)). On the other hand, the alloys containing Sn formed the Mg\(_{17}\)Al\(_{12}\) and Mg\(_{2}\)Sn phases along grain boundaries in Fig. 2(b)–(d). The Mg\(_{2}\)Sn phase has a similar shape with the Mg\(_{17}\)Al\(_{12}\) phase and was precipitated nearby the Mg\(_{17}\)Al\(_{12}\) phase. And with increase of Sn contents, the volume fraction of secondary phases was increased as plotted in Fig. 3.

3.2 Potentiodynamic polarization measurement

The typical electrochemical polarization curves of AZ51 alloys with different Sn additions after OCP is stable in a 3.5% NaCl solution are shown in Fig. 4. All the curves were not symmetrical between their anodic and cathodic branches. Much sharper changes were observed in the anodic polarization branches than in the cathodic branches. Interestingly, almost all the curves had the linear behavior almost to the value of the corrosion potential. But the reason for this remained unclear, the similar phenomenon was also observed in the other literatures.\(^{10,18}\)

Electrochemical corrosion data of all alloys are listed in Table 2. Comparing with AZ51 alloy, the alloys with Sn addition had a corrosion potential ranging from −1.50 to −1.45 V vs. Ag/AgCl, about 10–60 mV higher than that of AZ51 alloy. Especially, TAZ551 alloy revealed the highest the corrosion potential among the four alloys. In case of the variation of anodic current density, the Sn addition had a slight effect on decreasing the anodic current density at the same potential, indicating that the anodic process of corrosion reaction was slightly suppressed by the addition of Sn. It indicated that the presence of the Sn stabilized the Mg(OH)\(_2\) layers and elevated the resistance to hydrogen evolution in the salt solution, and thus the anodic current density was decreased.\(^{19}\) The easy discharge of hydrogen ions is considered as one of the major corrosion mechanism for magnesium, resulting in better corrosion performance if the discharge is suppressed.

The corrosion potentials measured on their respective polarization curves were slightly higher (30–70 mV) than
Fig. 2 SEM micrographs of the as-cast (a) AZ51, (b) TAZ151, (c) TAZ551, and (d) TAZ951 alloy microstructure. (e) and (f) show the EDS spectrums of secondary phase in Fig. 2(c).

Fig. 3 Volume fractions of secondary phase of AZ51 alloy by Sn addition.

Fig. 4 Potentiodynamic polarization curves of AZ51 alloys with and without Sn addition.
their open circuit potential (OCP) recorded after 30 min of immersion. The difference between their open circuit potential and corrosion potential was explained as follows: The cathodic polarization induced a modification of the surface composition with the formation of Mg(OH)$_2$ and MgH$_2$, which could limit the increase of the anodic current.

### 3.3 Immersion test and corrosion morphology

Figure 5 illustrates the effect of the Sn additions on corrosion rates of the AZ51 alloy immersed in 3.5% NaCl solution. The corrosion resistance of TAZ51 alloys was increased with the Sn contents up to 5 mass%, but on the contrary decreased when the Sn contents were 9 mass%.

The corrosion properties of magnesium alloy depended on the precipitates and galvanic corrosion potential. And in most cases, the improved corrosion resistance is principally attributed to this secondary phase. In the present study, the discrete Mg$_{17}$Al$_{12}$ and Mg$_2$Sn phases were mainly precipitated at the grain boundaries. The Mg$_{17}$Al$_{12}$ phase, which had a $-1.20\text{V vs. SCE}$ value of $E_{corr}$, was cathodic with respect to the matrix and more corrosion resistant compared to $\alpha$-Mg matrix.\cite{20} Although the $E_{corr}$ of Mg$_2$Sn phase was still unclear, it looks like the Mg$_2$Sn phase seems to be nobler than the $\alpha$-Mg matrix and behaves as a passive cathode. It indicated that these phases played a dual role in corrosion, depending on their volume fractions.\cite{12} It acts as an effective barrier when its volume fraction is high and the interparticle distance is not large as like in die-casting alloy. Hence, the oxide film on the phase is continuous so that the dissolution of $\alpha$-Mg matrix is inhibited. On the other hand, if the Mg$_{17}$Al$_{12}$ phase is coarse and interparticle distance is very high as like in gravity casting, the networking is not possible. In this case, the corrosion rate is increased by Mg$_{17}$Al$_{12}$ phase. Moreover, underlining of Mg$_{17}$Al$_{12}$ phase also occurs due to the corrosion of matrix near the phase.

Improvement in corrosion resistance of Mg-Al based alloy due to the alloying additions is reported in literature.\cite{21-23} The reasons attributed to such improvement are (i) refining of Mg$_{17}$Al$_{12}$ phase and formation of more continuous network, (ii) suppressing the formation of Mg$_{17}$Al$_{12}$ phase by forming another intermetallic with Al which is less harmful to corroding $\alpha$-Mg matrix and (iii) added elements may incorporate into the protective film and thus increasing its stability. In this study, it can be seen from the microstructure that the addition of Sn to AZ51 alloy does not change the size and morphology of Mg$_{17}$Al$_{12}$ phase. And it does not form any another compound with Al, but forms Mg$_2$Sn phase. When the contents of Sn were 5 mass%, the secondary phases formed semi-continuously along grain boundaries. Although Mg$_2$Sn and Mg$_{17}$Al$_{12}$ phase formed the semi-continuous structure, the effect of stabilization of Mg(OH)$_2$ layers by Sn additions caused the improvement of corrosion resistance of TAZ51 alloy. On the other hand, in case of TAZ951 alloy, secondary phases also formed the semi-continuous structure. There was the effect of inhibition of hydrogen evolution by 9 mass%Sn additions, however, the presence of too many cathodic phases caused much more galvanic sites, and thus the corrosion resistance was decreased. It could be postulated that the effect of enhanced inhibition of hydrogen evolution and stabilization of Mg(OH)$_2$ layers were the most effective on corrosion behavior of TAZ alloys up to 5 mass%Sn addition, and thus TAZ51 alloy showed superior corrosion resistance to other alloys.

In order to clear the influence of Mg$_2$Sn and Mg$_{17}$Al$_{12}$ phase on corrosion property of AZ51 alloy, the initial corrosion stage of TAZ51 and TAZ951 alloy was described in Fig. 6. Several regions with severe corrosion were observed at the $\alpha$-Mg/secondary phase interfaces due to the galvanic effect in Fig. 6(a). Indeed, it is known that localized corrosion is the most common form of corrosion for magnesium alloys in chloride-containing solutions. The TAZ alloys also were predominated over localized corrosion. In enlarged image Fig. 6(b), the initial corrosion preferentially occurred in surroundings of Mg$_2$Sn phase, not Mg$_{17}$Al$_{12}$ phase. It indicated that the galvanic potential differences between $\alpha$-Mg and Mg$_2$Sn phase is more larger than those of $\alpha$-Mg and Mg$_{17}$Al$_{12}$ phase. In short, it is postulated that the Mg$_2$Sn phase has a higher galvanic potential than Mg$_{17}$Al$_{12}$ phase.

X-ray diffraction patterns in the as-corroded surface of TAZ alloys after 2 h immersion test are shown in Fig. 7. It was analyzed the main corrosion products of TAZ alloys were Mg(OH)$_2$. According to other research, although unipositive Mg$^+$ and bipositive Mg$^{++}$ ion exist together in initial corrosion stage, the unipositive Mg$^+$ ion converts to the equilibrium Mg$^{++}$ ion either electrochemically or chemically because of the instability and insufficient lifetime of unipositive Mg$^+$ ion.\cite{24} In shortly, MgO formed in the early stages of the corrosion, while Mg(OH)$_2$ became dominant after longer time immersion because Mg(OH)$_2$ is more stable than MgO.\cite{25}
4. Conclusions

The microstructure and corrosion behavior of Mg-xSn-5Al-1Zn (x = 0, 1, 5 and 9 mass%) alloys was investigated. Main results were as follows:

(1) The AZ51 alloy was mainly composed of α-Mg and Mg17Al12 phase. On the other hand, the alloys with Sn addition consisted of α-Mg, Mg17Al12 and Mg2Sn phases. With the increase of Sn contents, the volume fraction of the secondary phases was increased.

(2) The corrosion resistance of TAZ alloys was increased in the up to 5 mass% Sn contents, but decreased in the alloys containing 9 mass% Sn contents. The effect of enhanced inhibition of hydrogen evolution and stabilization of Mg(OH)2 layers by the 5 mass% Sn additions caused a drastic decrease in corrosion rate. But, the corrosion resistance was decreased when Sn contents were 9 mass% because of too many galvanic sites by increased volume fraction of the Mg2Sn and Mg17Al12 phase.

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