CHAPTER SEVEN
PREDICTING GALVANIC CORROSION RATES FOR AZ61/SIC METAL MATRIX COMPOSITES IN NaCl

Observations made during the study on the galvanic-corrosion behaviour of Mg alloys reinforced with SiC particles were analysed using various de-aerated concentrations of NaCl by using the potentiodynamic polarisation techniques. Results showed that the composites became less prone to corrosion than the matrix alloy, which may be due to the presence of chemically inert SiC particles in the MMCs. The test also revealed that the corrosion resistance of both the alloy and composites decreased with the increase in concentration of NaCl. The SEM analyses were undertaken to clarify the effect of SiC particles on the corrosion mechanism.

7.1 Introduction

Metal matrix composites (MMCs), especially Mg MMCs, offer the designer many added benefits, since they are particularly suitable for applications requiring their combined high strength, better wear resistance, thermal conductivity, damping properties, and low coefficient of thermal expansion with lower density. These properties of Mg MMCs enhance their usage in automotive, aerospace and marine applications.

Mg MMCs are used in acidic media should have good mechanical properties and resistance to chemical degradation in acidic environment. It is therefore highly essential to have a thorough understanding of the corrosion behaviour of the Mg composites. Some authors have pointed out that the extent of pitting in SiC-Mg MMCs increased with increase in SiC volume fraction, which may be due to the
preferential acidic attack at the matrix-reinforcement interface. In other words some researcher, indicated that SiC additions do not appear to affect substantially pitting attack on some Mg alloys because, whilst pits were more numerous on the composite, they were smaller and shallower than those on unreinforced alloy. The corrosion behaviour of MMCs is influenced by the nature of matrix alloy, the type of reinforcement and the presence of alloying elements such as copper, magnesium, and silicon. In spite of all these factors, the corrosion behaviour of Mg MMCs is of complex nature.

This investigation was performed to determine the galvanic corrosion and corrosion mechanism of Mg coupled with SiC particles. Experiments were performed in deaerated 3.5, 0.35 and 0.035 % by weight of NaCl solution at lab temperature. In order to determine the effect of H₂ reduction and Mg passivity on galvanic corrosion behavior these environments were selected. The galvanic corrosion rate was estimated from the polarization diagrams, using tangential method. The microstructure of the surfaces was studied before and after corrosion test by using optical microscope and SEM technique.

7.2 Experimental Procedure

The electrochemical instrumentation Potentiostat-Galvanostat (model CL95), which is used in present study, consists of a function generator, and a graphic plotter. These devices are interfaced with a personal computer. The instrument consists of a Platinum Reference Electrode (RE), Calomel Electrode (CE) and Working Electrode (WE) and five-mouth flat bottom flask. The polished specimens were mechanically connected to copper holders (WE). One cm² area of the surface of the specimen was
exposed to the electrolyte and the rest of the surface was covered by Teflon tape. Before testing, each specimen was cleaned in methanol for five minutes and then air-dried. Meantime the test solutions of 0.035, 0.35 and 3.5 % deaerated NaCl solutions were prepared. In this test, the anodic and cathodic polarization was measured at a scan rate of 0.167mVs\(^{-1}\). The imposed potential Vs logarithmic current plot was obtained directly from the microcomputer. All potentials obtained were referred to as RE.

7.3 Results

7.3.1 Corrosion behaviour

Figures 7.1, 7.2 and 7.3 show the polarization curves for both Mg alloy and Mg/SiC MMCs, where potential is plotted vs. galvanic current for tests conducted in 3.5, 0.35 and 0.035 % of NaCl media respectively. Decrease in concentration of the NaCl solution, results in a marked increase in galvanic potential for both the composite and matrix alloy. This also indicated the development of higher electrical resistance in-between corrosion media and electrodes. Hence the corrosion resistance increased with increase in galvanic potential, which indicates that the corrosion rate decreased with decrease in concentration of corrosion media.

To determine the effect of concentration of NaCl on the corrosion current density (I\(_{\text{corr}}\)) rate, electro-chemical measurements were carried in 0.035, 0.35, and 3.5 % NaCl solution. Figures 7.1, 7.2, and 7.3 depicts Tafel polarization curves for both the unreinforced and reinforced Mg alloys. The cathodic and anodic curves of both alloy and composites are similar, but cathodic curve of composites has slightly shifted outward, which is attributed to decrease in chemical reaction between the electrode and electrolyte. The concentration had a marked effect on the corrosion rate of all the
Fig. 7.1 Polarization diagrams of SiC reinforced MMCs exposed to deaerated 3.5% N of NaCl scan rate 0.16 mVs⁻¹.
Fig. 7.2 Polarization diagrams of SiC reinforced MMCs exposed to de aerated 0.35% N of NaCl at the scan rate 0.16 mVs⁻¹.
Fig. 7.3 Polarization diagrams of SiC reinforced MMCs exposed to de aerated 0.035% N of NaCl at the scan rate 0.16 mVs⁻¹.
samples. With increase in normality of NaCl solution, \( I_{\text{cor}} \) also increased as shown in Table 7.1. The corrosion current was found to be proportional to the rate of hydrogen gas evolution.

### 7.3.2 Effect of normality of the solution

Also the shape of the polarization curves depends on the concentration of NaCl. It is well known that the chemical reaction depends on the concentration of solution, area of the reaction surfaces, etc. The intensity of the corrosion attack increased with increase in concentration; on the same line some researchers\(^{83-84}\) attributed this trend to the intensity of Cl\(^-\) concentration of the solution, which increases corrosion rate.

The point of intersection between the cathodic and anodic curves gives \( I_{\text{cor}} \). The corrosion rate was calculated using conversion formula\(^{85}\).

\[
\text{Corrosion rate in mpy} = CE_w \frac{I_{\text{cor}}}{d} \tag{1}
\]

Where \( C \) is the conversion constant (=1.287 X10\(^5\)), \( E_w (=\text{atomic weight of specimen/valence electrons}) \) is the equivalent weight of the sample (g), \( d \) is the density of the sample (g/cc\(^3\)) and \( I_{\text{cor}} \) is A/cm\(^2\).

Table 7.1 shows corrosion rate vs. of normality of NaCl solution and percentage of reinforcement. For all specimens irrespective of the presence of SiC reinforced, the corrosion rate increased with increase in the concentration of NaCl solution. An increase in the wt. % of SiC particulate exhibited lesser corrosion rate than that of matrix alloy.
7.3.3 Effect of reinforcement

Table 7.1. $I_{cor}$ and corrosion rate of MG alloy and Composites

<table>
<thead>
<tr>
<th>Normality of NaCl</th>
<th>Wt.% of SiC reinforced MG composites</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>$I_{cor} (\text{mA/cm}^2)$</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>146</td>
</tr>
<tr>
<td>0.35</td>
<td>35</td>
</tr>
<tr>
<td>0.035</td>
<td>12</td>
</tr>
</tbody>
</table>

Corrosion rate, $10^6 \text{ mpy}$

<table>
<thead>
<tr>
<th>Normality of NaCl</th>
<th>3.5</th>
<th>0.35</th>
<th>0.035</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^6 \text{ mpy}$</td>
<td>62.6</td>
<td>15</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>43.7</td>
<td>12.9</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>35.6</td>
<td>6.4</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>35.2</td>
<td>3.4</td>
<td>2.6</td>
</tr>
</tbody>
</table>

From Table 7.1 it can be clearly observed that the ceramic reinforcement particles remains inert in aggressive chloride media. It is one of the reasons for decrease in corrosion rate with increase in SiC content. The extent of exposure of the MMCs area to aggressive Cl⁻ environments in corrosion testing was found to lead to lesser corrosive reaction than that of the matrix alloy. The polarization curve of both MMCs and reinforcement are similar in nature with slight potential changes. It is also observed that Hydrogen evolution slightly decreases with increase in weight percentage of the reinforcement.
Fig. 7.4 Comparison of the $I_{\text{cor}}$ and corrosion rate vs. % of SiC reinforced with Mg alloy composites
7.4 DISCUSSION

In the present investigation, Mg alloy contains mainly two phases of primary Mg and eutectic silicon. It also contains precipitates like Mg$_2$Si, AlFeSi$_8$, CuAl$_2$ [FeMn] SiAl$_8$ compound, etc. when the alloy is prepared. This alloying precipitate enhanced conductivity at the inter-metallic phase, which provides an easier path for the electron exchange necessary for hydrogen reduction. Since silicon is less-active, it cannot convert hydrogen ions to hydrogen gas, in general silicon gets positive values for its standard reduction electrode potential. Al usually gets negative sign for its listed electrode potential, which is more reactive than hydrogen and can reduce hydrogen ions to hydrogen gas. Hence Silicon permits Mg to function as anode by under going de-electronation or oxidation reaction. It is generally known that the addition of alloying elements like Cu and Si shifts the corrosion potential in the noble direction and reduces the corrosion resistance of Mg$^{89-90}$. Badawy et. al$^{91}$ explained in their report that increasing copper content decreases the corrosion resistance of the Mg alloy. In addition to all the above elements, the MG alloy, which are strongly anodic to the matrix results in higher corrosion rate due to the formation of local cell.

In the case of MG/SiC composites, the SiC is a ceramic; it is chemically inert in both alkali and acidic solutions. The reinforcement acts as a physical barrier for the corrosion reactions and also it reduces area of the matrix alloy to react in the media. The presence of the reinforcement phase decreases the corrosion current density, which is further retarded by additional reinforcement$^{92}$, it may also increase the bonding strength of the matrix and reinforcement. The bonding strength avoids the crack getting developed in the MMCs due to corrosion, which may also be one of the reasons for the increase in the corrosion resistance.
One more reason for the decreasing corrosion rate of the composite is the interface of reinforcement and matrix, which becomes the site of corrosion. It is due to the formation of magnesium inter-metallic layer adjacent to the particle during manufacture as discussed by Trzaskoma\textsuperscript{93}. McIntyre et al\textsuperscript{94-95} further showed that the magnesium inter-metallic compound is more active than the alloy matrix. Pitting in the composites is associated with the particle-matrix interface, because of the higher magnesium concentration in this region. With increase in pitting corrosion would continue to occur at random sites on the particle-matrix interface. The active nature of the crevices would cathodically protect the remainder of the matrix and restrict pit formation and propagation. On the same line, Badawy et al\textsuperscript{96} explained that of presence of small amount of Mg in Al alloy improves the passivation behavior of the alloy, which increases the corrosion resistance.

7.5 CONCLUSIONS

- The corrosion behaviour of anodized MG MMCs was studied using electrochemical techniques.
- Concentration of solution plays a significant role in the corrosion of given MMCs.
- $I_{\text{corr}}$ of both the composites and alloy increased with increase in concentration of the NaCl solution.
- The extent of corrosion rate (mpy) was decreased with increase in weight percentage of reinforcement.
- The use of MMCs in structural applications in marine environment is more suitable than that of the matrix alloy.