Chapter 7

Development of Zn-SiC composite coatings and their corrosion behavior.
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7.1. Introduction:

Zinc has been utilized as a sacrificial layer to defend steel from corrosion. However, the life span of zinc coating is limited in aggressive corrosive environment. Consequently, considerable efforts are being made to improve their corrosion resistance property along with other mechanical and physical properties. One of the possible solutions for this is the incorporation of inert particles (nano or micro sized) into a growing Zn metal matrix during electrodeposition. The resulted coatings generally referred to as metal matrix composite and it has attracted interest due to its unique functional properties such as corrosion resistance and wear, hardness, magnetic and semiconductor properties compare to pure metal coating [1, 2].

The nanoparticles like TiO$_2$ [3], ZrO$_2$ [4], MoS$_2$ [5], CeO$_2$ [6], CNT [7] and SiO$_2$ [1] were used to prepare Zn metal matrix composite and their mechanical and electrochemical behavior have been studied. According to literature, SiC nanoparticles were used to fabricate Ni-SiC composite coatings and their mechanical and corrosion behavior have been reported [8-10]. Swiderska-Sroda et al. used SiC nanoparticles to generate Zn-SiC composite coatings and analyzed their surface appearance [11]. But till now there is no reports on the evaluation of corrosion behavior of Zn-SiC composite coatings. Hence the present work is mainly focused to generate Zn-SiC composite coatings by means of electrodeposition method. The fabricated coatings were characterized by SEM, EDX, SEM cross section and XRD analysis. The corrosion behavior of the coatings was analyzed by Tafel polarization and Electrochemical Impedance studies.
7.2. Results and Discussion:

7.2.1. Deposition of Zn-SiC composite coatings:

The plating bath mentioned in the Table 7.1 was used to generate Zn-SiC composite coatings. 1, 2, 3 gL\(^{-1}\) of SiC nanoparticles of size 64.28nm were suspended in plating electrolyte by means of mechanical stirring and sonication in order to generate composite coatings. The Zn-SiC composite coatings were deposited by applying 0.04 Acm\(^{-2}\) current density under the operating conditions given in Table 7.1. Obtained coatings were named as Z (Zn+0 gL\(^{-1}\) of SiC), ZS\(_1\) (Zn+1 gL\(^{-1}\) of SiC), ZS\(_2\) (Zn+2 gL\(^{-1}\) of SiC) and ZS\(_3\) (Zn+3 gL\(^{-1}\) of SiC)

Table 7.1. Bath composition and operation conditions.

<table>
<thead>
<tr>
<th>Bath composition</th>
<th>Concentration</th>
<th>Operating conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSO(_4)</td>
<td>200 gL(^{-1})</td>
<td>Anode: Zinc plate (99.99% pure)</td>
</tr>
<tr>
<td>Na(_2)SO(_4)</td>
<td>10 gL(^{-1})</td>
<td>Cathode: Mild steel plate</td>
</tr>
<tr>
<td>H(_3)BO(_3)</td>
<td>8 gL(^{-1})</td>
<td>Current density: 0.04 Acm(^{-2})</td>
</tr>
<tr>
<td>CTAB</td>
<td>0.05 gL(^{-1})</td>
<td>Plating time: 10 min</td>
</tr>
<tr>
<td>SiC</td>
<td>1, 2 &amp; 3 gL(^{-1})</td>
<td>Stirring speed: 300 rpm, pH:3.5, Temperature: (27 \pm 2 ^\circ)(\text{C})</td>
</tr>
</tbody>
</table>

7.2.2. Electrochemical measurements:

a) Tafel Polarization:

The Tafel polarization measurements were conducted to evaluate the stability of coatings towards the aggressive media. The polarization patterns were recorded after 30 min immersion in 3.5% NaCl corrosive media and are depicted in Fig. 7.1. The corrosion kinetic parameters such as corrosion potential (\(E_{corr}\)), corrosion current density (\(I_{corr}\)), cathodic (\(\beta_c\)) and anodic (\(\beta_a\)) Tafel slopes were calculated from the curves and are tabulated in Table 7.2.
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**Fig. 7.1.** Tafel polarization curves of Zn and Zn-SiC coatings in 3.5 % NaCl solution.

**Table 7.2.**  
Electrochemical kinetic parameters of the coatings derived from Tafel plots.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$E_{\text{corr}}$ in V</th>
<th>$I_{\text{corr}}$ in $\mu$A cm$^{-2}$</th>
<th>$\beta_c$ mV dec$^{-1}$</th>
<th>$\beta_a$ mV dec$^{-1}$</th>
<th>Corrosion rate $\mu$g h$^{-1}$ cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>-1.047</td>
<td>8.505</td>
<td>280</td>
<td>35.72</td>
<td>10.06</td>
</tr>
<tr>
<td>ZS$_1$</td>
<td>-0.995</td>
<td>2.802</td>
<td>248</td>
<td>32.80</td>
<td>3.314</td>
</tr>
<tr>
<td>ZS$_2$</td>
<td>-0.989</td>
<td>2.215</td>
<td>182</td>
<td>32.92</td>
<td>2.620</td>
</tr>
<tr>
<td>ZS$_3$</td>
<td>-1.000</td>
<td>3.526</td>
<td>192</td>
<td>36.69</td>
<td>4.170</td>
</tr>
</tbody>
</table>

The corrosion potential of the composite coatings shifted towards less negative potential with decrease in corrosion current density compare to pure Zn deposit. This is attributed to the better anticorrosive nature of the Zn-SiC composite coatings. Among composite coatings ZS$_2$ deposit shown better corrosion resistance than ZS$_1$ and ZS$_3$. This may due to the defects, dislocations and chemical heterogeneities formed on the zinc deposit because of the second phase particles and also due to the agglomeration of SiC nanoparticles in plating bath solution.
b) Electrochemical Impedance Study:

Impedance measurement is the most useful and informative method to assess the corrosion behavior of metal coating. They are capable of in situ and non-destructively probing relaxation phenomena over a wide frequency range. The impedance data are presented as Nyquist plots (Fig. 7.2) and typical bode plots (Fig. 7.3).

Fig. 7.2. Nyquist plots corresponds to Zn and Zn-SiC composite coatings.

Fig. 7.3. Bode plots corresponds to Zn and Zn-SiC composite coatings.
Three capacitive loops correspond to corrosion process are observed in the Nyquist and Bode plots. The analysis of shape of the impedance spectra with the fitted electrical equivalent circuit (EEC) help to understand the electrochemical process occurring at the surface. This means that obtaining a good fit does not imply that the used model is correct. Whereas the shape of the spectra is influenced by electrochemical process at the surface and/or by the geometric factors of electrode [12]. Hence to obtain impedance parameters, the experimentally determined EIS data were fitted with 3RC equivalent circuit (Fig. 7.4) (which possess lower % of error) with the help of ZSimpWin 3.21 software. To get appreciable fitting results the employed low and middle frequency capacitance element (C) in EEC was replaced by constant phase element (CPE). The impedance of CPE is defined by the following equation

\[ Z(j\omega) = (Q)^{-1} (j\omega)^n \]

where \( Q = \) CPE constant \( j = \) imaginary unit,
\( \omega = \) angular frequency \( (\omega=2\pi f ; f = \text{frequency}) \)
\( n = \) CPE exponent \((-1 \geq n \leq 1)\).

The CPE exponent ‘n’ is a measure of capacitance dispersion, for an ideal capacitor \( n=1 \) and if there is decrease in ‘n’ value means the non uniform distribution of current arises from the surface roughness and surface defects [13-16].

In the circuit (Fig. 7.4) each element is attributed to the following contributions [17-20].
\( R_e \) is the electrolyte resistance appeared between the reference electrode and the surface of the coated specimen. i.e., working electrode.
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The high frequency contribution \((C_f - R_f)\) is ascribed to the dielectric character of the thin surface layer formed from the corrosion products \((C_f)\) and its electrical leakage from ionic conduction through its pores \((R_f)\).

The medium frequency contribution is attributed to the double layer capacitance \((Q_{di})\) at the electrolyte / coated surface interface at the bottom of the pores coupled with the charge transfer resistance \((R_{ct})\). This charge transfer resistance is closely related to corrosion rate.

The low frequency couples \((Q_F - R_F)\) may related to a redox process taking place at the surface likely involving the thin layer of corrosion products accumulated at the electrolyte / working electrode interface.

![Electrochemical equivalent circuit](image)

Fig. 7.4. Electrochemical equivalent circuit employed to simulate EIS data.

The corrosion parameters calculated from the EEC simulation are tabulated in Table 7.3. The polarization resistance \((R_p)\) value of the coatings were calculated by adding \(R_d\), \(R_{ct}\) and \(R_F\) i.e. \(R_p = R_d + R_{ct} + R_F\). The ZS\(_2\) composite coating exhibited high \(R_p\) value which is attributed to good corrosion resistance property. However, ZS\(_1\) and ZS\(_3\) composite coatings also showed good anticorrosive behavior compared to pure Zn coating.
Table 7.3.
Electrochemical corrosion parameters obtained from EEC simulation.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>(C_d) in (\mu\text{Fcm}^{-2})</th>
<th>(R_d) in (\Omega\text{cm}^2)</th>
<th>(Q_d) in (10^{-6}) ((\Omega\text{cm}^2\text{S}^{-1}))</th>
<th>(n_d)</th>
<th>(R_{ct}) in (\Omega\text{cm}^2)</th>
<th>(Q_F) in (10^3) ((\Omega\text{cm}^2\text{S}^{-1}))</th>
<th>(n_F)</th>
<th>(R_F) in (\Omega\text{cm}^2)</th>
<th>(R_p) in (\Omega\text{cm}^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>6.913</td>
<td>2.851</td>
<td>86.05</td>
<td>0.812</td>
<td>401.3</td>
<td>4.884</td>
<td>0.931</td>
<td>91.69</td>
<td>495.84</td>
</tr>
<tr>
<td>ZS_1</td>
<td>9.883</td>
<td>6.106</td>
<td>15.06</td>
<td>0.874</td>
<td>2188</td>
<td>0.270</td>
<td>0.729</td>
<td>1546</td>
<td>3740.10</td>
</tr>
<tr>
<td>ZS_2</td>
<td>5.107</td>
<td>21.32</td>
<td>8.479</td>
<td>0.793</td>
<td>4280</td>
<td>1.004</td>
<td>0.887</td>
<td>1670</td>
<td>5971.32</td>
</tr>
<tr>
<td>ZS_3</td>
<td>3.415</td>
<td>31.17</td>
<td>3.365</td>
<td>0.865</td>
<td>1658</td>
<td>0.773</td>
<td>0.787</td>
<td>591.5</td>
<td>2280.67</td>
</tr>
</tbody>
</table>

\(*R_p = R_d + R_{ct} + R_F*

The electrochemical studies indicated that Zn-SiC composite coatings showed much lower activity towards external aggressive media than pure Zn deposit.

7.2.3. Characterization and surface analysis:

The results obtained from the electrochemical studies shows that the corrosion behavior of the composite coatings was improved when compared to pure zinc coating. it may due to the changes in physical and chemical properties of the deposit because of incorporation of the SiC nanoparticles. To support the results from electrochemical studies and to know the incorporation of SiC nanoparticles in to zinc matrix, the obtained deposits were subjected to characterization and surface analysis.

The cross sectional SEM image (Fig. 7.5) and the EDX (Fig. 7.6) data recorded on the cross section of the deposit confirms the incorporation of SiC nanoparticles in zinc metal matrix. The SiC content in the deposit is given in Table 7.4. According to Table 7.4, the SiC content in the deposit was slightly varied with respect to the particle loading in plating bath. High content of Si was observed in the deposit ZS_2.
Fig. 7.5. SEM cross section image of ZS$_2$ composite coating.

Fig. 7.6. EDX pattern of ZS$_2$ composite coating.

Table 7.4.
Wt % of different elements present in the deposits obtained from EDX analysis.

<table>
<thead>
<tr>
<th>Wt %</th>
<th>ZS$_1$</th>
<th>ZS$_2$</th>
<th>ZS$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>1.93</td>
<td>1.98</td>
<td>2.01</td>
</tr>
<tr>
<td>Si K</td>
<td>0.30</td>
<td>0.33</td>
<td>0.32</td>
</tr>
<tr>
<td>Zn K</td>
<td>97.77</td>
<td>97.69</td>
<td>97.67</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

The SEM surface images of the Zn and Zn-SiC composite coatings are given in Fig. 7.7. In pure zinc coating, the randomly distributed hexagonal zinc platelets were observed. Meanwhile, in composite coatings, hexagonal zinc platelets
were well stacked and are parallel to the substrate, also refinement in grain size was observed. The SiC nanoparticles were also observed on the surface of the deposit. These particles may act as the barrier to protect the deposit from corrosion by minimizing the local defects on the surface of the deposit.

**Fig. 7.7.** SEM images of Zn and Zn-SiC composite coatings.

**Fig. 7.8** shows the surface SEM images of Zn and Zn-SiC composite coatings after Tafel polarization study. During anodic polarization the corrosion process takes and the zinc is etched away slowly leaving SiC particles on the metal surface. This hinders the further dissolution of zinc metal. But in pure zinc deposit, the zinc undergoes dissolution continuously with same or at accelerated rate. However, the inclusion of SiC nanoparticles in to zinc matrix brings down the corrosion rate of the zinc. Also less number of corrosion products were noticed on composite coatings surface when compare to pure zinc coating.
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The XRD patterns of zinc deposit obtained in absence and presence of SiC nanoparticles is shown in Fig. 7.9. In XRD patterns, the peak corresponds to SiC nanoparticles were not observed. This may due to the little incorporation of SiC nanoparticles in to Zn matrix.

![XRD pattern of deposits Z, ZS1, ZS2 and ZS3.](image)

**Fig. 7.9.** XRD pattern of deposits Z, ZS1, ZS2 and ZS3.
The average crystallite size of the deposits was calculated using XRD data and Scherer equation (Eq. 3.3) and is tabulated in Table 7.5. The average crystallite size of the composite coatings (in particular ZS₂) is minimum when compared to pure zinc coating. Because, the embedded nanoparticles reduced the zinc crystal growth by providing more surface area for fresh nucleation [4, 5]. Hence the average crystallite size of the composite coatings gets reduced.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Z</th>
<th>ZS₁</th>
<th>ZS₂</th>
<th>ZS₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average crystallite size in nm</td>
<td>89.95</td>
<td>94.69</td>
<td>48.80</td>
<td>114.76</td>
</tr>
</tbody>
</table>

By using XRD data and Eq. 3.4, the Texture co-efficient (Fig. 7.10.) of the deposits was calculated in order to know the influence of SiC nanoparticles on the preferred orientation of zinc crystals. In pure zinc coating (1 0 0) plane was dominated, but it is changed to (0 0 2) and (1 0 1) planes in composite coating. This reveals that the incorporated SiC nanoparticles changed the preferred orientation of the zinc crystals and made them to exhibit better anticorrosive property.

![Texture Co-efficient](image)

**Fig. 7.10.** Preferential orientation of Zn crystallites of Zn coating Z and Zn-SiC composite coatings ZS₁, ZS₂ and ZS₃.
All the results gathered above, confirm that the obtained composite coatings were fine grained, compact, free from local defects and are covered by SiC nanoparticles on their surface. These improved structural properties may lead to improve the corrosion resistance property which was observed from electrochemical analysis.

7.3. Conclusion:

The Zn-SiC composite coatings were successfully generated on steel by electrodeposition method. The results obtained from electrochemical corrosion studies reveal that, Zn-SiC composite coatings have better corrosion resistance property than pure zinc coating. EDX and XRD studies confirmed the incorporation of SiC nanoparticles in zinc matrix. The SEM and preferred orientation analysis shows that the morphology of zinc deposit was changed because of the embedded SiC particles. The incorporated SiC nanoparticles bring down the average crystallite size of the deposit and also uniform and compact nature was observed in composite coatings. These morphological changes provide improved anticorrosive property to the zinc deposit.
References:


[12] Fabio La Mantia, Jens Vetter and Peter Novak. Impedance spectroscopy on Porous materials: A general model and application to graphite electrodes of
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