Chapter-6.2

Effect of surfactants on Zn-Ni/MWCNTs coatings

Electrostatic Stabilization

Steric Stabilization
Effect of surfactants on Zn-Ni/MWCNTs composites and corrosion behavior

6.2.1. Introduction

The success of codeposition and corresponding properties of composites are dependent on various factors including particle size and their concentration in the bath. The primary objectives of composite coatings like corrosion, wear and friction resistance, hardness, lubricity etc. can be greatly improved by increased incorporation of the particulate matters [1-2].

In literature, different surfactants are utilized to enhance the particle incorporation. Ionut Zamblan et al., [3] electrodeposited Cu-SiO$_2$ nanocomposite in the presence of Cetyltrimethylammonium bromide (CTAB). This cationic surfactant played a beneficial role in SiO$_2$ suspension stabilization and promoting the codeposition of nanoparticles to the deposit. They showed higher corrosion resistance of the composite. Chao Guo et al., [4] examined the effect of surfactants on electrodeposition of nickel-CNT composite coatings. The results showed that anionic surfactant sodium lauryl sulfate (SLS) slightly decreased but CTAB increased the codeposition of CNTs in the coatings. Ming-Der Ger [5] observed a high percentage of uniformly distributed SiC particles in nickel matrix in the presence of CTAB. CTAB, which a cationic surfactant developed a positive charge on the surface of the particles and increased adhesion between particles and cathode, enhancing possibility of embedding particles. A redox surfactant azobenzene was used by Nabeen K Shrestha et al., [6] in nickel-diamond composite coatings. The surfactant played a key role in deagglomerating the particles which results in higher reinforcement.
Chapter 6.2  
Zn-Ni/MWCNT composites: Effect of Surfactants

In the case of codeposition of CNTs, uniform dispersion of CNTs in the bath and good suspension is the key factor for getting good coatings. The CNTs can be kept dispersed by various means like mechanical agitation, ultrasonication and by using surfactants. The dispersion of CNTs in the bath can be studied via UV-Vis spectroscopy. Bundle CNTs are not active in this region. Hence, dispersion can be characterized by using UV-Vis absorption spectroscopy and it is possible to establish a relationship between the amounts of CNTs individually dispersed in solution and the intensity of the corresponding absorption spectrum. In the present work, different surfactants are used in the Zn-Ni electrodeposition. Their effect on particle dispersion, morphology, crystal structure and corrosion resistance are evaluated.

6.2.2. Experimental

Sample preparation

Analytical reagents and distilled water were used to prepare the plating solution. The composition of the electrolyte is given in table 1. The multiwalled carbon nanotubes (MWCNT), purchased from Sigma Aldrich India were used as received without any further treatment.

The surfactants cetyltrimethylammonium bromide (CTAB) (cationic), sodium lauryl sulfate (SLS) (anionic) and Triton-X were used in the study. The three concentrations of each surfactant were used. The solution was stirred with 1200 rpm speed for 12h followed by ultrasonication. The UV-Visible spectroscopy was used to study the dispersion of the particles in different conditions.

Absorptions were recorded in the region 200nm to 800nm. Base line correction was carried out using pure solutions containing MWCNTs without any surfactants. Zn-Ni-CNT composite coatings were prepared with experimentally found
Table 6.2.1 Bath composition and parameters.

<table>
<thead>
<tr>
<th>Bath</th>
<th>MWCNT</th>
<th>CTAB</th>
<th>SLS</th>
<th>Triton X</th>
<th>Deposit code</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>BB</td>
<td>25 mg/L</td>
<td>-</td>
<td>-</td>
<td>C₀</td>
</tr>
<tr>
<td>II</td>
<td>BB</td>
<td>25 mg/L</td>
<td>-</td>
<td>-</td>
<td>C₇</td>
</tr>
<tr>
<td>III</td>
<td>BB</td>
<td>25 mg/L</td>
<td>0.425 mM</td>
<td>-</td>
<td>Cᵦ</td>
</tr>
<tr>
<td>IV</td>
<td>BB</td>
<td>25 mg/L</td>
<td>-</td>
<td>4.05 mM</td>
<td>Cₗ</td>
</tr>
<tr>
<td>V</td>
<td>BB</td>
<td>25 mg/L</td>
<td>-</td>
<td>0.12 mM</td>
<td>Cᵦᵦ</td>
</tr>
</tbody>
</table>

BB (Basic bath) composition: ZnSO₄ · 6H₂O – 160 g/L, NiSO₄ · 7H₂O – 24 g/L, Na₂SO₄ – 40 g/L, H₃BO₃ – 8 g/L.

optimum surfactant concentration. Electrodeposition process was carried out with pH 2.5 at current density 3 A/dm² for 10 min duration.

6.2.3. Results & discussion

6.2.3.1. Coating characterization

Fig. 6.2.1 shows the SEM images of the ZnNi deposits of the thickness around 12 – 14 μm obtained under different conditions. The ZnNi deposit without any additives shows coarse-dull deposit having randomly distributed nano-laminated thin hexagonal platelets. The composite coating without any surfactant was homogeneous. When the composite coating was fabricated in the presence of surfactants, morphology was coarser to some extent compared with that of the composite C₇ without any surfactant. This may be due to the low concentration of CNTs or smaller CNTs to surfactant ratios. The CNT concentration was about 0.8 wt.% in C₇, however it increases in the presence of surfactants. The particle content was found to
be 1.24 wt.% and 1.9 wt.% in the coating fabricated with CTAB and Triton-X. However, CNT incorporation was maximum of 4.4 wt.% in solution of SLS.

![SEM images of different ZnNi coatings.](image)

**Fig. 6.2.1.** SEM images of different ZnNi coatings.

![XRD analysis and Texture coefficients for the ZnNi coatings.](image)

**Fig. 6.2.2.** XRD analysis and Texture coefficients for the ZnNi coatings.
Chapter 6.2  

Zn-Ni/MWCNT composites: Effect of Surfactants

Fig. 6.2.2 displays XRD patterns of the Zn-Ni alloy deposits. These diffractograms clearly indicate crystalline nature of the deposits. Grain sizes of the deposits were calculated from Debye Scherrer equation. The grain size of the deposit C₀ was found to be 39 nm and that of C₁ was 32 nm. However, the composites generated in the presence of different surfactants, CTAB and SLS were of grain sizes 22 and 28 nm respectively, whereas as with TritonX, Zn-Ni had 34 nm.

The effect of surfactants on preferred orientation was studied by calculating texture coefficients [7-8] and it is represented in Fig. 5.1.4b. From the graph, it is noticed that, majority of the crystallites were oriented parallel to (1 0 1) plane in pure Zn-Ni coating. The CTAB orients the crystallites parallel to (1 0 0) and SLS to (0 0 2), (1 0 2) and (1 1 0) preferred orientation. TritonX influences the crystallization to grow parallel to (1 0 1) plane.

6.2.3.2. UV-Vis spectroscopic studies

Individual CNTs are active in the UV–Vis region and exhibit characteristic bands corresponding to additional absorption due to 1D van Hove singularities. Bundled CNTs, however, are hardly active in the wavelength region between 200 and 1200 nm – their photoluminescence is quenched – most probably because of carrier are tunneling between the nanotubes. Bundle carbon nanotubes are not active in the UV-Vis region, only individual carbon nanotubes absorb in this region. Hence, dispersion of CNTs can be characterized using UV-Vis absorption spectroscopy. Therefore it is possible to establish a relationship between the amounts of CNTs in solution and the intensity of the corresponding absorption spectrum [9]. To characterize the dispersion of MWCNTs in plating bath solution, UV-Vis spectroscopy and absorbance values are used. Fig. 6.2.3 depicts UV-vis spectra of
MWCNTs with varying concentration of CTAB, SLS and Triton-X surfactants in ZnNi plating bath solutions.

**Fig. 6.2.3.** UV-Vis absorption spectra for CNTs in bath solution with different surfactants.

The graphs showing the absorbance clearly depict the effect of surfactants on the dispersion of CNTs in the bath solution. It can be clearly seen that, with the increase in surfactant concentration the dispersion also increases. By reaching CMC value, no surfactant shows further enhancement in the CNT dispersion. At CMC or higher
concentrations, surfactant molecules form micelles in solution. In other words at higher concentrations of surfactants, portions of surfactants extend into the liquid phase and interact with each other. This interaction causes flocculation and decreases the dispersion of nanotubes at high surfactant concentration [2]. So there is an optimum ratio that the quality of nanotubes dispersion deteriorates above this ratio. TritonX is found very effective towards dispersing of the CNTs compared to CTAB and SLS. This may be because of large polymeric molecular size of the TritonX.

6.2.3.3. Electrochemical studies

The electrodeposited ZnNi alloy coatings were evaluated for their corrosion resistance in 3.5% NaCl solution. Fig. 6.2.4 shows the Tafel extrapolation curves for the ZnNi coated samples. The CNT incorporated composite samples found to be shifted towards higher positive potential values. Table 6.2.2 presents the data obtained from Tafel experiments. Incorporation of CNTs makes the composite makes more noble compared to plain ZnNi alloy film. The composite coatings deposited in the presence of surfactants found to have more resistance towards corrosion. The composite C_Cs emerged as highly noble, with high R_p and least I_corr value compared to C_CT and C_CC.

The EIS technique was also used to evaluate the electrochemical behavior of the deposits. The table 6.2.3 displays the impedance data obtained for the coatings. The Nyquist diagrams in Fig. 6.2.4.a give the information about the extent of protection ability of different coatings. The electrochemical equivalent circuit shown in Fig. 6.2.4.b was to study the behavior. The two semi circles in the Nyquist loops and two humps in the Bode plot (log(f) vs. phase angle) confirms nature of the process to be of two relaxations.
Fig. 6.2.4. Tafel curves for ZnNi coatings in 3.5% NaCl solution.

Table 6.2.2 Corrosion data obtained from Tafel experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\beta_p$ V$^{-1}$</th>
<th>$\beta_a$ V$^{-1}$</th>
<th>$R_p$ V$^{-1}$</th>
<th>$I_{corr}$ V$^{-1}$</th>
<th>Corrosion rate g/h</th>
<th>$E_{corr}$ V</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_0$</td>
<td>5.3</td>
<td>16.5</td>
<td>1007</td>
<td>1.98x10$^{-5}$</td>
<td>2.41x10$^{-5}$</td>
<td>-1.081</td>
</tr>
<tr>
<td>$C_C$</td>
<td>6.7</td>
<td>16.5</td>
<td>1199</td>
<td>1.56x10$^{-5}$</td>
<td>1.91x10$^{-5}$</td>
<td>-1.072</td>
</tr>
<tr>
<td>$C_{CC}$</td>
<td>5.9</td>
<td>17.2</td>
<td>1399</td>
<td>1.34x10$^{-5}$</td>
<td>1.64x10$^{-5}$</td>
<td>-1.059</td>
</tr>
<tr>
<td>$C_{CT}$</td>
<td>5.4</td>
<td>24.1</td>
<td>1499</td>
<td>1.05x10$^{-5}$</td>
<td>1.29x10$^{-5}$</td>
<td>-1.048</td>
</tr>
<tr>
<td>$C_{CS}$</td>
<td>3.7</td>
<td>20.5</td>
<td>1780</td>
<td>1.008x10$^{-5}$</td>
<td>1.23x10$^{-5}$</td>
<td>-1.039</td>
</tr>
</tbody>
</table>

With the incorporation of MWCNTs, the composite $C_C$ shows wider Nyquist loop compared to $C_0$ indicating higher corrosion resistance. However, the composites with different surfactants show longer Nyquist curves inferring higher polarization resistance. From the table, variation in the values of capacitances can be observed with the nature of coatings. Proposed equivalent circuit consists of two sets of RCs.
Fig. 6.2.4 a) Nyquist diagram, b) Equivalent circuit and c) Bode plots for the ZnNi systems in 3.5% NaCl solution.

High frequency elements are related to dielectric character ($C_{\text{col}}$) of the coating that is reinforced by the ionic conduction through its pores ($R_{\text{col}}$). Further, low frequency elements can be attributed to the double layer capacitance ($C_{\text{dl}}$) at the coating electrolyte interface at the bottom of the pores coupled with charge transfer...
Table 6.2.3 Corrosion data obtained for EIS technique for ZnNi coatings 3.5% NaCl solution.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$C_{cot}$ F/cm$^2$</th>
<th>$C_{dzi}$ F/cm$^2$</th>
<th>$R=R_{cot}+R_{ct}$ Ω cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_0$</td>
<td>$6.2\times10^{-6}$</td>
<td>$7.5\times10^{-5}$</td>
<td>572</td>
</tr>
<tr>
<td>$C_C$</td>
<td>$4\times10^{-6}$</td>
<td>$5.7\times10^{-6}$</td>
<td>650</td>
</tr>
<tr>
<td>$C_{CC}$</td>
<td>$3.1\times10^{-6}$</td>
<td>$5.0\times10^{-5}$</td>
<td>1019</td>
</tr>
<tr>
<td>$C_{CT}$</td>
<td>$3.0\times10^{-6}$</td>
<td>$0.2\times10^{-6}$</td>
<td>1272</td>
</tr>
<tr>
<td>$C_{CS}$</td>
<td>$2.67\times10^{-6}$</td>
<td>$0.1\times10^{-7}$</td>
<td>1419</td>
</tr>
</tbody>
</table>

resistance ($R_{ct}$). With the increase in $R_{cot}$, values of $C_{cot}$ decrease suggesting passivation becoming less permeable. However, the decline in $C_{dzi}$ values with higher $R_{ct}$ advocates decreased active surface area directly in contact with the corrosion medium as a consequence of compact structures.

From the experimental evaluation, it can be signified that the role played by surfactants. It is observed that, inclusion of particles in $C_C$ made resistive than $C_0$. It should be noted that, the composites prepared with the surfactants show betterment in the protection ability [10-14]. UV-Vis spectroscopic studies inferred that, in the presence of TritonX MWCNTs show high absorbance and it was most successful in deagglomeration than CTAB and SLS. But EDX analysis reports the particle content was highest in the presence of SLS (4.4 wt.%) compared to that of CTAB (1.24 wt.%) and TritonX (1.9 wt.%). SLS not only increased the particle codeposition but also significantly modified the surface morphology to finer grained and compact. The grain size of the deposit $C_{CS}$ was found to be 28 nm which provide lesser grain boundaries from where initiation of dissolution is expected. Furthermore,
Chapter 6.2  

Zn-Ni/MWCNT composites: Effect of Surfactants

High MWCNT reinforcement made the coating to be highly corrosion resistant with minimized exposure to corrosive environment.

6.2.4. Conclusion

The Zn-Ni coatings and CNT composites were electrodeposited successfully. To enhance the dispersion of the CNTs in the bath different surfactants were used. To evaluate the dispersion strength of surfactants, UV-Vis spectroscopy was utilized. In the presence of optimum concentration of TritonX CNTs were dispersed to higher extent. But it could not modify the ZnNi surface significantly. SLS fine grained the coating and aided to incorporate the nanoparticles to higher extent. This made the composite coating in the presence of SLS to be highly corrosion resistant in 3.5% NaCl solution.

References


