Chapter-5.1

Zn/nano CeO$_2$ composite coatings
Electrochemical studies on Zn/nano CeO$_2$ electrodeposited composite coatings

5.1.1. Introduction

The nano ceria is used as an antioxidant and also it possesses low thermal conductivity and higher thermal expansion coefficient [1]. In recent years ceria is used as gas sensors, electrode material for solid oxide fuel cells, oxygen pumps, amperometric oxygen monitors and abrasive for chemical mechanical polishing slurry. Ceria, in glass industry is considered to be the most efficient glass polishing agent. It is very important to note that cerium compounds either as coatings [2] or as inhibitors [3-4] are known to polarize the cathodic reactions thereby slowing down oxidation of the substrate [7-8].

The CeO$_2$ has been made use to fabricate composite coatings with nickel metal. Incorporation of CeO$_2$ nanoparticles to metal matrix enhanced wear and corrosion resistance, microhardness and improved high temperature oxidation resistance [4-8]. The authors reported that the composites of desired properties may be prepared by proper choice of the electrodeposition parameters and the particles concentration in the electrolytes.

The composite coating of zinc with CeO$_2$ was studied via hot dip process by Shibli et al., [2] and they reported that the corrosion resistance was improved considerably. In our present study electrodeposition of zinc was carried out and CeO$_2$ nanoparticles were introduced to metal matrix. The effect of Cetyltrimethylammonium bromide (CTAB), a cationic surfactant on the composite
properties was studied. This cationic surfactant is expected to increase the particle incorporation and affect the corrosion behavior of the composites.

The coatings’ morphology, structure along with electrodeposition process and corrosion behavior is studied in detail.

5.1.2. Experimental

Analytical reagents and distilled water were used to prepare the plating solution. The composition of the electrolyte is given in table 5.1.1. The CeO₂ (Cerium (IV) oxide, nanopowder <25nm (BET), purchased from Sigma Aldrich were used as received without any further treatment. For good dispersion and disaggregation of particles, the solution was stirred magnetically with 1200 rpm speed for 12h before electrochemical experiments.

Table 5.1.1. The plating bath composition and parameters.

<table>
<thead>
<tr>
<th>Bath constituents</th>
<th>Bath parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSO₄.7H₂O - 180g/L</td>
<td>pH = 2.5</td>
</tr>
<tr>
<td>Na₂SO₄ - 30g/L</td>
<td>Current density - 4 A/dm²</td>
</tr>
<tr>
<td>NaCl - 10g/L</td>
<td>Temperature - 25±2°C</td>
</tr>
<tr>
<td>CTAB - 0.5mM</td>
<td></td>
</tr>
<tr>
<td>CeO₂ - 0.5,1, 2.5g/L</td>
<td></td>
</tr>
</tbody>
</table>

The electrodeposition experiments were performed under a constant current density of 4 A/cm² and the deposition time was 20 minutes. [Sample codes: Cₐ - Zinc, Cₐ - Zinc-CTAB, Cₖ - Zn-0.5g/L CeO₂, Cₜ - Zn-1g/L CeO₂, Cₜ - Zn-2.5g/L CeO₂, C₉ - Zn-CTAB-0.5g/L CeO₂, C₁₀ - Zn-CTAB-1g/L CeO₂, Cₙ - Zn-CTAB-]
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Throughout the composite deposition process the electrolyte was stirred at a speed of 300 rpm.

5.1.3. Results and Discussion

5.1.3.1. Particle size distribution and zeta potential

The Fig. 5.1.1 shows the size distribution statistic for the CeO₂ particles in zinc plating bath (Cₑ and Cₕ) in the absence and presence of CTAB, which was stirred magnetically 12h before use. This composite electrolyte was immediately used to measure the size distribution. Size distribution of this magnetically homogenized composite electrolyte resulted with different population of the particles. Here it produces polydispersed colloidal system with poly dispersity factor 0.29 (the factor less than 0.02 points the system is monodisperse). Also the sample quality 2.4 (in the scale of ten set by the manufacturer of the instrument) shows that the autocorrelation functions were calculated very well. To maintain the bath stability and smaller diameter of the CeO₂ particles in plating bath the deposition experiments were carried out at constant stirring conditions.

![Fig. 5.1.1. The CeO₂ nanoparticles size distribution statistics for the bath Cₑ (a) and Cₕ (b) at 1200 rpm.](image)

The maximum volume of CeO₂ distributed was with around 122.5 nm in the presence of CTAB. This distribution was almost 130 nm without surfactant in the
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bath. Thus the cationic surfactant present in the bath solution diminishes the agglomeration and aids to homogenous distribution of the particles. This infers the effect of surfactant on the size distribution of the nanoparticles.

In principle solid particles when come into aqueous interface tend to polarize and show electrical charge. The nature and magnitude of the charge are function of pH and the nature of electrolyte. It is also reported in literature that by adsorption of zinc ions on the particle surface at a pH near to the isoelectric point of the particles increases the positive charge of the suspended particles [9]. To know the adsorption of the charged species on particles, zeta potentials in the presence and absence of CTAB at constant pH have been found out. The CeO₂ nanoparticles possess the surface charge of -4.08mV in the zinc bath solution. But the addition of 0.5mM of CTAB drastically shifts the zeta potential to +5.5mV.

5.1.3.2. SEM

The Fig. 5.1.2 depicts the surface morphology of the zinc electrodeposits. The image C₄ shows, the zinc deposit in the absence of any additive. It can be easily seen that, zinc deposit displays the hexagonal zinc plates aligned parallel to the substrate. The arrangement of hexagonal platelets can be clearly noticed.

From the SEM pictures corresponding to Zn-CeO₂ composite coatings with CeO₂ concentrations 2.5g/L (C₅) we can observe the agglomerated and localized CeO₂ nanoparticles in the zinc matrix. The surface morphology of Zn-CeO₂ composite in the presence of CTAB surfactant is also represented in the Fig. 2. The introduction of CTAB to the electrolyte changes the morphology to needle shaped, fine grained and uniform nature. The smaller grain size advocates the modification on the competition
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between nucleation and crystal growth. It is noteworthy that, needle shaped morphology results in porous nature of the coating. The increase in nuclear number and needle growth can be attributed to the strong blocking effect of cationic surfactant CTAB [14]. The increased CeO₂ bath loads have shown the higher incorporation of particles. Moreover, the incorporated particles are no longer agglomerated and concentrated at a particular region. So the porous nature of the zinc matrix has been reduced resulting in compact and uniform deposit.

Fig. 5.1.2. SEM images of the coatings.

5.1.3.3. Surface roughness

Surface roughness of the 15 μm thick electrodeposits has been evaluated using stylus profilometer. The Fig. 5.1.3 shows the roughness values for the deposits. The zinc deposit exhibits a higher roughness among all other coatings. This is because of the random distribution of nano-laminated thin hexagonal platelets developed in the
absence of any additives parallel to the substrate surface [15]. The Zn-CeO\(_2\) composite coatings show a trend of decreasing roughness with the increased addition of CeO\(_2\); however, the decrease is marginal. The incorporated nano-CeO\(_2\) decreased the non-uniformity by accumulating at the grain boundaries. The zinc deposit in the presence of CTAB has transformed to a needle shaped smooth morphology and decreased the surface randomness. This morphological changeover leads to a large decrease in the roughness. Further, the composites prepared with CTAB, showed better uniform surface nature. The added CeO\(_2\) may have filled up the pores and porous nature of the deposit aroused due to the addition of CTAB could have been diminished.

Fig. 5.1.3. Graph showing surface roughness measurement values for different samples Ca - Zinc, Cb - Zinc-CTAB, Cc - Zn-0.5g/L CeO\(_2\), Cd - Zn-1g/L CeO\(_2\), Ce - Zn-2.5g/L CeO\(_2\), Cf - Zn-CTAB-0.5g/L CeO\(_2\), Cg - Zn-CTAB-1g/L CeO\(_2\), Ch - Zn-CTAB-2.5g/L CeO\(_2\).
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5.1.3.4. XRD – Texture

Fig. 5.1.4a displays the X-ray diffractograms obtained for hexagonal zinc deposits obtained for the coatings $C_a$, $C_b$, $C_e$ and $C_h$. It signifies the effect of surfactant and nanoparticles on crystallographic orientation and crystallinity of the deposits.

![XRD patterns](image)

Fig. 5.1.4a. XRD patterns for the coatings $C_a$, $C_b$, $C_e$ and $C_h$.

The development of different crystal structures can be related to the surface energy differences which become driving force for the relative growth of grains which have lowest surface energy and (002) plane is the lowest surface free energy owing to its compactness [14]. The coating $C_a$ the bare zinc and the specimen $C_e$ which is Zn-CeO$_2$ 2.5g/L composite without surfactant preferentially orient in (002) plane indicating no significant effect of CeO$_2$ particles on the crystal structure.

The surface morphologies of the deposits $C_b$ and $C_h$ have been modified in the presence of CTAB. The intense peaks in the presence of CTAB are (100) and (110). The marked decrease in the basal (002) plane intensity is due to the modification of
metal's surface energy by the adsorption of the organic molecules. The various interactions of the molecules with different crystal planes induce different growth mechanisms. And, increased surface energy can be held responsible for the deviation of hexagonal crystal structure with the addition of CTAB. The incorporation of CeO$_2$ nanoparticles in the zinc matrix can be verified through the peaks obtained at 20 values at around 56 and 63 with (104) and (302) respectively in the deposit $C_h$ (Ref. JCPDS card no. #441001).

The determination of textures of the deposits is of very interest as the electrocrystallization of zinc is very sensitive to the bath composition. The preferred orientations of the deposits were determined using Muresan's method calculating the texture coefficients ($T_c$) [24]. The preferred crystallographic orientation is indicated by a $T_c$ value larger than unity and represented graphically in Fig. 5.1.4b. From the graph, it is clear that, in the absence of any additives, majority of Zn oriented parallel to (002) plane and this is almost same with the sample containing CeO$_2$ particles ($C_e$).

In the presence of CTAB, preferred orientation changes to (100) plane. This is altered with the 2.5% load of CeO$_2$ particles into (110) plane. This signifies the participation of CeO$_2$ in codeposition and its effect on the structure of the zinc deposit.

As the additives are added to the solution, they are adsorbed on the electrode affecting the crystallographic orientations of the deposits. The polarization of cathodic potentials in the presence of additives (CTAB and CeO$_2$) further supports the above discussion.
5.1.3.5. Cathodic polarization

To study the effect of CeO$_2$ particles on the reduction process during the electrodeposition, cathodic polarization profiles were recorded for blank solutions without zinc metal ions both in the presence and absence of CTAB.

From the Fig. 5.1.5a it can be seen that for blank solution the cathodic current is due to hydrogen reduction and the possible reduction reactions hydrogen evolution reactions (HER) [25] are given by Eqs. (1) and (2)

$$H_2O^+ + 2e^- \rightarrow H^+ + OH^- \quad (1)$$

$$2H_2O + 2e^- \rightarrow H_2 + OH^- \quad (2)$$

The addition of CeO$_2$ to the blank solution cannot cause any new process but they create some blockage on the electrode for the HER to occur. The adsorption of CeO$_2$ particles on the cathode suggests that CeO$_2$ which were dispersed in the blank...
solution are transported to electrode surface. Many factors like electrophoresis (positive surface charge), mechanical entrapment (by continuous stirring), adsorption (physically/weak forces) and convection, diffusion etc. may have been influenced for the CeO$_2$ transport to the cathode. The electrokinetic measurements suggests that CeO$_2$ particles are positively charged below pH 4.43 [23] and this will help to drift towards the cathode (electrophoresis). The possible reduction reaction pathway on cathode [17] is given in eqs (3) and (4).

\[ CeO_2.H^+ + e^- \rightarrow CeO_2.H_{ads} \]  
(3)

\[ CeO_2.H_{ads} + H^+ + e^- \rightarrow CeO_2 + H_2 \]  
(4)

With the increased concentration of CeO$_2$ in the plating bath the reduction current decreased indicating the blockage of more number of active sites on the cathode thereby quenching the hydrogen evolution. The reduction current for the bath solution without CeO$_2$ was high compared to those electrolytes having all the three concentration of the particles. This effect found to be a function of concentration of CeO$_2$. This result advocates the adsorption of particles on the electrode reducing the active surface area, in the conditions of the blank solution. Further, the similar experiments were carried out in the presence of surfactant CTAB. With the introduction of 0.5g/L of CeO$_2$ to the blank solution containing CTAB, the current densities due to HER were minimized. Obviously, further increase in the particles concentration leads to the decrease in the reduction current without distinct difference in the polarization curves.
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Fig. 5.1.5a. Cathodic polarization curves on steel electrode for the blank solutions (I) without CTAB and (II) with CTAB.

In literature it is reported that the metal ion Me²⁺ electrodeposition takes place in several steps. It is believed that an intermediate Me⁺ adsorbed on the electrode during cathodic reaction. During electroreduction the localized concentration of hydroxide ions in close proximity to the cathode surface will increase and consequences in the formation of MeOH_ads. The probable chemical reaction path of zinc ions reduction in acidic medium is specified below [17].

\[
\begin{align*}
Zn^{2+} + H_2O \rightarrow (ZnOH)^{2+} + H^+ & \quad \text{(5)} \\
(ZnOH)^{2+} + e^- \rightarrow Zn(OH)_{ads} & \quad \text{(6)} \\
Zn(OH)_{ads} + e^- \rightarrow Zn + OH^- & \quad \text{(7)} \\
Zn(OH)_{ads} + (ZnOH)^{+} + 2e^- \rightarrow Zn + OH^- + Zn(OH)_{ads} & \quad \text{(8)}
\end{align*}
\]
**Fig. 5.1.5b.** Cathodic polarization curves for the deposition of Zinc from different bath solutions.

The Fig. 5b presents the cathodic polarization behavior for zinc electrolyte. From the zinc solution, reduction of the Zn$^{2+}$ ions to Zn can occur at around -1.086V vs. SCE. But CTAB polarizes the zinc reduction and deposition occurs at higher negative potentials at -1.14V with simultaneous fall in the current. The polarization profiles I and II, in Fig. 5.1.5b, presents the effect of CeO$_2$ particles on deposition process with and without surfactant. The CeO$_2$ nanoparticles polarize the deposition process to negative potentials in absence of surfactant. The adsorbed nanoparticles to the cathode block the surface thereby decreasing the zinc reduction current [17, 19-21]. It is interesting to note that, particles depolarize the deposition process in the presence of CTAB with small rise in the cathodic current [17, 22]. This observation is due to higher rate of reduction of zinc ions in comparison with the hydrogen evolution which is in accordance with the results obtained by Gomes et al. [19]. Also, this can be attributed to the possible increase in ionic transport by nanoparticles in the presence of CTAB. A reasonable explanation is that the adsorption of surfactant molecules increases the particle surface positive charge density and probably strengthens the
adsorption strength between particles and cathode surfaces. The results are coincident with profile (c) in Fig. 5.1.5b, wherein CeO₂ particles promote the deposition of Zn. Furthermore, the zeta potential obtained from solutions containing CTAB is more positive than that for solutions containing particles with no CTAB at the same metal ion concentration.

5.1.3.6. Electrochemical studies

The polarization measurements were carried out in a potential range of ±200 mV vs. OCP to aid mechanistic understanding of the influences of CTAB and different concentrations of CeO₂.

Fig. 5.1.6a. Tafel curves for different zinc samples in 3.5 wt.% NaCl solution.

The equation relates to the corrosion behavior of the metal, which freely and uniformly corrodes in a homogeneous medium. The physical and chemical heterogeneity (presence of defects/dislocations or CeO₂ particles or impurities) of the zinc coating disturbs the electrochemical electrode reactions, which as a result may
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proceed faster in some places while being inhibited in other places. The Tafel plots registered for various zinc specimens are showed in Fig. 5.1.6a. The graph 5.1.6b which shows the variation of Rp and CR (corrosion rate), depicts the protection ability of different deposits in 3.5% NaCl solution. It can be clearly noted that, Rp values are higher for the composites with increased concentrations of Ceria. But these values further enhanced in the presence of CTAB. However, the corrosion rates decreased with higher CeO$_2$ bath load. The beneficial effect of CeO$_2$ incorporation on corrosion rates more

![Graph](image)

**Fig. 5.1.6b.** The graphical representation of polarization resistances and corrosion rates obtained from Tafel experiments.

pronounced when the composites were deposited using CTAB. This can be illustrated by the lower protection ability of Zn-CeO$_2$ with 2.5g/L compared to the same composite prepared with surfactant. Moreover, the Zn-CTAB-CeO$_2$ with 1g/L of bath load resists more than that of the composite prepared with 2.5g/L without CTAB.
An equivalent circuit consisting of 2 RC circuits shown in the inset of Fig. 5.1.7 was proposed [23]. The two loops in the Nyquist diagrams shown in Fig. 5.1.7 indicate that the process consists of two relaxations or it is of two time constants. All the diagrams are of same nature differing only in their point of intersection with the $Z_{\text{real}}$ axis which is being quantitative characteristic of corrosion resistance.

The parameters generated from impedance studies are shown in table 5.1.2. The composites in the presence of CTAB show higher $R_{\text{cot}}$ compared to those without surfactant, whereas the $C_{\text{cot}}$ values decrease suggesting that the passivation is less permeable than in the absence of surfactant. These high frequency elements are related to the dielectric character ($C_{\text{cot}}$) of the coating that is reinforced by the ionic conduction through its pores ($R_{\text{cot}}$). Further, the low frequency contribution is attributed to the double layer capacitance ($C_{\text{dl}}$) at the coating electrolyte interface at
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the bottom of the pores coupled with the charge transfer resistance $R_{ct}$. For the composite coatings with CTAB, $R_{ct}$ increases while the $C_{dl}$ decreases. This decline in $C_{dl}$ values could be attributed to a decrease in active area directly in contact with the corrosion medium as a consequence of compact structures.

Table 5.1.2. Parameter values for various zinc coatings obtained from Electrochemical impedance studies in 3.5 wt.% NaCl solution.

<table>
<thead>
<tr>
<th>Coatings</th>
<th>$C_{cot}$ $\mu$F/cm$^2$</th>
<th>$C_{dl}$ mF/cm$^2$</th>
<th>$R_p=R_{cot}+R_{ct}$ $\Omega$ cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_a$</td>
<td>13.84</td>
<td>0.9061</td>
<td>241.44</td>
</tr>
<tr>
<td>$C_b$</td>
<td>12.2</td>
<td>0.5092</td>
<td>688.43</td>
</tr>
<tr>
<td>$C_c$</td>
<td>9.129</td>
<td>0.2525</td>
<td>1144.87</td>
</tr>
<tr>
<td>$C_d$</td>
<td>4.057</td>
<td>0.2245</td>
<td>1394.9</td>
</tr>
<tr>
<td>$C_e$</td>
<td>0.6722</td>
<td>0.0224</td>
<td>1470.8</td>
</tr>
<tr>
<td>$C_f$</td>
<td>0.473</td>
<td>0.0124</td>
<td>1868.6</td>
</tr>
<tr>
<td>$C_g$</td>
<td>0.4359</td>
<td>0.0094</td>
<td>2263.87</td>
</tr>
<tr>
<td>$C_h$</td>
<td>0.4057</td>
<td>0.0002</td>
<td>2533.31</td>
</tr>
</tbody>
</table>

The corrosion morphologies for four coatings $C_a$, $C_b$, $C_e$ and $C_h$ obtained after immersion in 3.5 wt.% NaCl solution for 75h is depicted in Fig. 5.1.8. The pure zinc coating shows very high deteriorated surface. The dissolution of the zinc layer is very high showing its poor corrosion resistance. The dissolution of zinc layer is controlled in the presence of surfactant because of the lower grain boundaries. The composite $C_e$ is better controlled from the corrosion due to the presence of inert nanoparticles which act as a barrier at the solution electrode interface. The coating $C_h$ containing both surfactant and particles is intact and there could be hardly corroded regions or pits seen. The surface being very compact it is well protected from corrosion.
The corrosion trend obtained from electrochemical experiments advocate the effect of cationic surfactant CTAB on the uniform distribution of incorporated CeO$_2$ nanoparticles in the metal matrix. Usually, the corrosion process proceeds along the grain boundaries. When CeO$_2$ particles are embedded in the zinc matrix, the corrosion path is hindered and the corrosion progresses preferentially along Zn-CeO$_2$ interface. Since ceria itself is having corrosion resistance [7], the corrosion resistance of the composite is much higher and thus the sacrificial protection of zinc coating is enhanced.

The prolonged protection by Zn-CeO$_2$ coatings produced in the presence of surfactant can be owed to the effect of CTAB on deposition process, surface nature and structure. The influence of cationic CTAB has been well illustrated by previous reports [24]. According to their model, the partial coverage of electrode surface by
the additive blocks the active sites, decreasing the nucleation rate affecting the nucleation mechanism. Thus in the presence of CTAB, the crystallization of zinc with hexagonal platelets is retarded and deposit turns to needle shaped, uniform but porous to some extent with the absence of larger grain boundaries. The zinc composites in the presence of CTAB exhibit higher corrosion resistance. The needle shaped deposit facilitates higher incorporation and uniform distribution of ceria. Moreover, the surfactant plays a major role in dispersing the secondary materials in the electrolyte. Its adsorption on particles develops a net positive charge (+5.5 mV) which assists the movement of the particles towards the cathode and favors the particles codeposition [17, 20, 25]. Also, the probability of higher incorporation of ceria nanoparticles in the presence of CTAB shows better corrosion resistance in the corrosive medium chosen for study as the electrode surface area to be exposed to corrosive environment decreases. The additives can be held responsible for good chemical stability of the composites, CTAB being cathodic polarizer, surface modifier and ceria which is being a pore filler forming a barrier at solution-electrode interface.

The Zn-CeO₂ 2.5g/L shows some lower corrosion resistance compared to that of Zn-CTAB-CeO₂ 1g/L. It may be because of the higher agglomeration and lower dispersion of particles in the electrolyte leading to the localized and non-uniformly incorporated particles. But the higher amount of particles in the presence of CTAB can effectively participate in the codeposition process and uniformly distributed within the zinc metal matrix. This argument can be well supported by the particle size distribution in the electrolyte with and without surfactant, Fig. 5.1.1. This is the most probable reason for the coating Cₙ to possess very high protection ability.
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5.1.4. Conclusion

The Zn-CeO₂ composites were successfully prepared from sulfate bath onto the mild steel substrates. The surfactant molecules and CeO₂ particles involve in deposition process and significantly affect surface morphology. The surfactant changed the preferred orientation of the deposition to (101) plane, which can be attributed to its adsorption on cathode surface. The change in preferred orientation leading to morphological modification facilitates good codeposition of nano ceria. Moreover, good dispersion and possession of positive charge aided by the surfactant result both in higher incorporation as well as uniform distribution of CeO₂ in the metal matrix. The CeO₂ incorporated zinc deposits perform well against corrosion. But the presence of surfactant makes it more successful. The composite coating derived from the bath containing lower concentration of particles with CTAB shows higher corrosion resistance compared to the coating fabricated from higher bath load without surfactant. Thus this study imparts the knowledge of fabrication of Zn-CeO₂ by electrodeposition technique and their electrochemical behavior proving nano-CeO₂ to be a good additive in the presence of CTAB.

References


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