Generation and Corrosion Behavior of Zn-Nano Sized Carbon Black Composite Coating

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A composite film of zinc and carbon black was electrodeposited on mild steel using zinc electrolyte containing dispersed nano sized carbon black. The corrosion behavior of the coating was studied in (3.5 wt%) NaCl solution by electrochemical and mass loss measurements. The study revealed porous free nature and higher corrosion resistance property of composite coating. The service life of coatings was estimated from the results of salt spray test. The surface morphology was investigated by recording the scanning electron microscopy (SEM) images of coating before and after corrosion. The grain size of coating was calculated by XRD images. Microhardness of the coating was measured. SEM and XRD studies inferred the reduction in crystalline size of composite coating.

1. INTRODUCTION

Electrodeposition process of generating composite coating is highly advanced method in material science as it produces new materials at room temperature and appropriately it is referred as cold fusion. Another important application over the other methods is its ability to produce co-deposit of metal with metallic, non metallic, polymers, ceramic, oxides, nano particles etc. The demand for metal matrix composites is always increasing due to their potential applications in all sectors[1-5]. In addition the composite coatings especially with nano particles have certain superior mechanical and metallurgical property which finds extensive use in corrosion control.

The zinc coating is widely employed on steel to control the corrosion process [6-8]. Zn-Alloy coatings exhibited higher corrosion resistance property than pure zinc coating [9,10]. Still there is growing interest in developing technological and economical viable route to improve the corrosion resistance property of zinc – alloy coating. The composite coatings containing Zn and nano particles

like carbon nano tubes, nano sized carbon paste, nano particles of TiO_2 , silica, SiC , ceramic powders, Fe_2O_3 etc are gaining importance due to their exiting corrosion resistance property [11,12]. The properties of Zn- nano material composites can be tuned to desired level by controlling the amount of nano particle in the deposit and by adjusting the electrochemical parameters of the deposition process. The electrochemically generated composite coatings of zinc and carbon nano tubes showed excellent corrosion resistance to aggressive chloride media. Similar studies on $Zn-TiO_2$, Zn – Carbon particle revealed that these nano composite gives protection to steel against corrosion [13,14].

The aim of present work is to generate zinc-nano sized carbon black composite from an electrolyte containing zinc ions and carbon black nano particles. Also it is aimed to know the corrosion behavior of the composite coating by performing chemical and electrochemical experiments.

2. EXPERIMENTAL PART

Pure zinc and composite coating were electro deposited on steel from sulphate bath. The constituents of the bath were 200g/L $ZnSO_4$, 50g/L Na_2SO_4 , 40g/L NaCl, 1.5g/L cetyl trimethyl ammonium bromide and 2.0g/L carbon black. The mean diameter of carbon black particles was in the range 5 -10nm. The SEM image and XRD spectra of carbon black are given in figure 1 and figure 2 respectively. Analytical grade chemicals and distilled water were used to prepare the plating solution. The bath solution (200 ml) was subjected to magnetic stirring at 200 rpm for 4 hours before plating. The mild steel and zinc plates were used as cathode and anode respectively for plating. The mild steel specimens were polished mechanically, and degreased by trichloroethylene in degreaser plant. The degreased cathodes were immersed in 10% HCl solution for few minutes followed by water wash. The zinc (anode) surface in each experiment was activated by dipping in 10% HCl for few seconds followed by washing with water. The same surface area of anode and cathode was used for electrodeposition process. The bath temperature was 300 K and pH was 3.5. The current density for plating was 3.5 A/dm^2. The electrodeposition process under galvanostatic condition using a regulated DC power source was carried out.
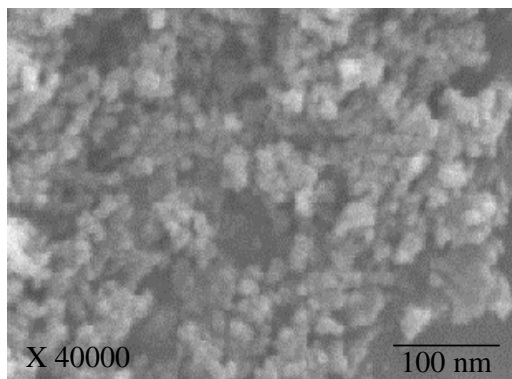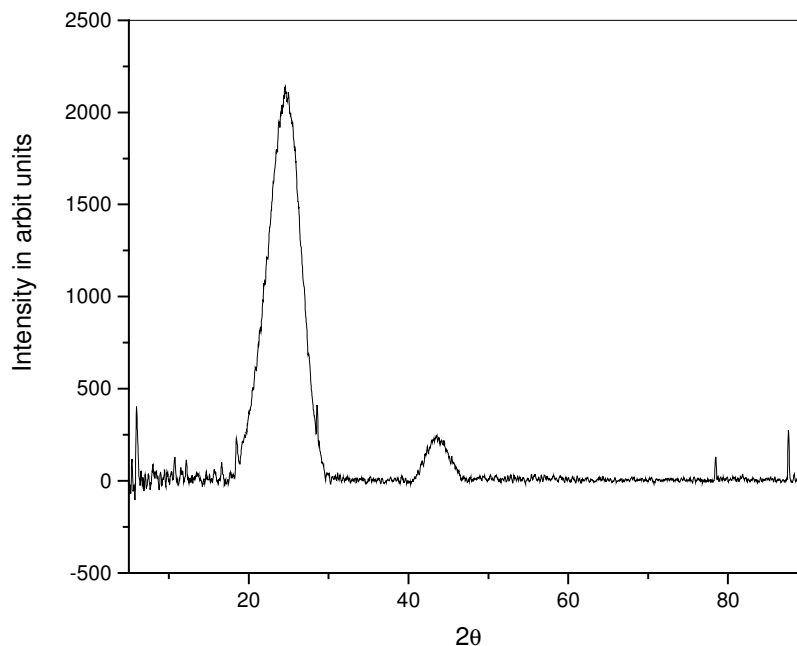

Figure 1. SEM image of carbon black

Figure 2. XRD Spectrum of carbon black

The electrodeposited mild steel plates of 2 X 2 cm^2 with pure zinc and Zn – carbon black composite were used for investigating their corrosion behavior by weight loss method. The composite coating was obtained on steel specimens from different electrolytes containing known amount of carbon black nano-particles. The corrosion experiments were performed by immersing coated samples in 3.5% NaCl solution. The weight loss of the deposit for a known period of immersion was measured and corrosion rate was determined.

A conventional three-electrode cell was used for polarization studies. The steel sample coated, with pure zinc or Zn – carbon black nano-particles with surface area of 1 cm^2 was employed as working electrode. Saturated calomel and platinum wire were used as reference and counter electrode respectively. The electrolyte was 3.5% NaCl solution. The electrochemical measurements were performed using AUTOLAB from Eco-Chemie made Netherlands. The polarization curves at a sweep rate of 0.1 mV/s were recorded. The electrochemical impedance measurements were recorded in the frequency range from 100 M Hz to 10 m Hz with ± 5 mV AC amplitude sine wave generated by a frequency response analyzer. Cyclic voltametric studies were performed in the same cell with mild steel as working electrode. The mild steel was polished successfully with 1.0, 0.3 and 0.05 μm alumina slurries and then cleaned ultrasonically with doubly distilled, deionised water. In this study electrolyte was sulphate bath with or without carbon black was employed.

The porous nature of the coated specimens were examined by adopting porosity test .The steel samples of pure zinc coated and composite coated samples of 5 X 5 cm^2 area were taken for this study. The deposit with thickness higher than 5 μm were porous free.

The salt spray test as per ASTM B 117 was carried out by following the standard procedure [15]. The test was conducted by spraying 5% NaCl solution vapors on coated articles hanged freely in

a closed chamber. The drops from the fog of NaCl get accumulated on the surface of the articles and facilitate the corrosion process resulting in the formation of zinc salts called white rust. The number of hours required in the formation of white rust was the indication of the corrosion resistance. The higher corrosion resistance property of the coating delays the formation of white rust and increases the service life of articles. The specimens' surfaces were observed carefully and the duration of time for the formation of white rust was noted.

The Vickers microhardness of the deposit was determined by an indentation technique with a weight of 50g for 10 seconds using Clemex microhardness tester, made in Japan. The average of five replicated values was recorded.

The morphology study of the surface of coated samples, before and after corrosion tests, was undertaken by scanning electron microscopy (SEM). The phase structure of the nano composite coating was analyzed on X ray diffractometer (XRD) and by using these data crystal size was also calculated.

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements

The Fig. 3 shows the weight loss measurement profiles of pure zinc coated and zinc composite coated samples, which were subjected to forced corrosion process in NaCl medium. The weight loss was maximum in pure zinc coated sample and it was reduced to half in the composite coated sample. The weight loss reduction in composite coatings shows good reinforcing action of carbon black and it was easily embedded in zinc matrix[16]. This hinders the easy dissolution of zinc. So corrosion rate was decreased in composite coating.
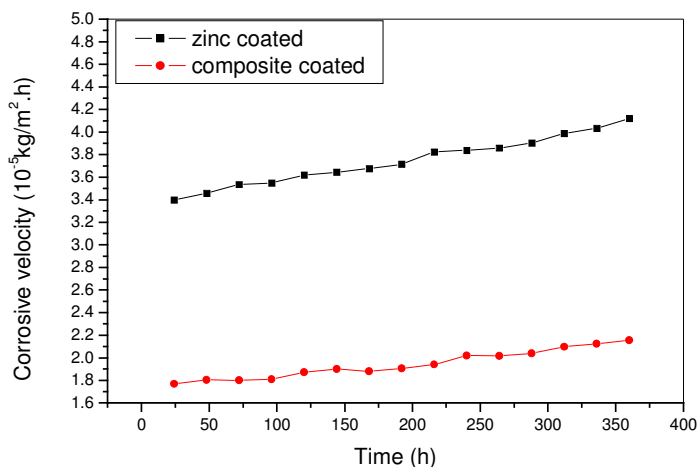

Figure 3. Corrosion rate with immersion time for pure zinc coating and composite coating samples in 3.5.% NaCl solution

3.2. Salt spray test

The industrial method of examining the corrosion behavior and to estimate the service life of zinc-plated objects was salt spray test. In the present study the white rust appeared after 20 hours on pure zinc coating and the Zn- carbon black composite showed the white rust after 40 hours. This test also provides an additional support and confirms the enhancement of corrosion resistance property of zinc in the presence of carbon black in its coating.

3.3 Electrochemical measurements

The anodic polarization curves of pure zinc and composite coated samples were shown in Fig. 4. The potential of composite coated sample was more positive in the entire current density region when compared to pure zinc coated sample except in the beginning. In zinc coated sample the current density values increases sharply at the potential region -1.01V (w r t SCE). In case of composite coated sample there is no such sharp raise increment in current density values but it was gradual. It indicated that metal dissolution take place continuously at lower potential values in zinc coated sample whereas in composite coated sample dissolution of metal take place at higher anode potential. Further there was steady increase in current density inferring steady increase in dissolution rate of metal.
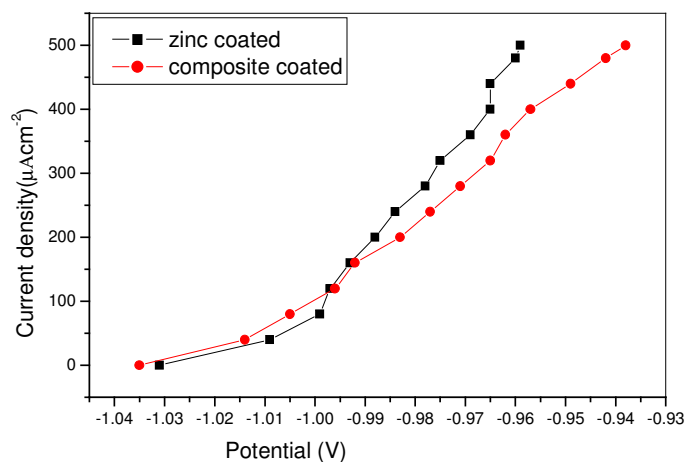

Figure 4. Anodic polarization curves for pure zinc coating and composite coating samples in 3.5 % NaCl solution.

The impedance diagram of composite coated and zinc coated samples are shown in Fig. 5. The Rp value of composite coated article was 27 and 20 for zinc coated sample. The C_{dl} values of composite coated sample was1.5 X 10^{-5} against 1.7 X 10^{-5} F cm^{-2}. The dissolution process was more pronounced in pure zinc coated than composite coated sample. This result indicated that incorporation of carbon black offers higher resistance for dissolution of zinc.
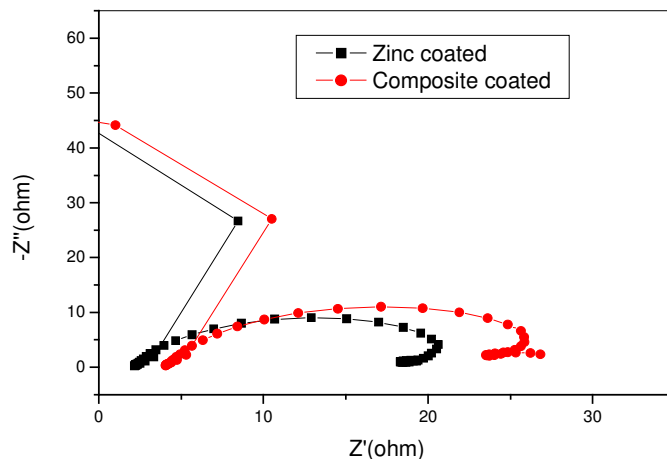
Figure 5. Impedance diagrams for pure zinc coating and composite coating samples in 3.5 % NaCl solution
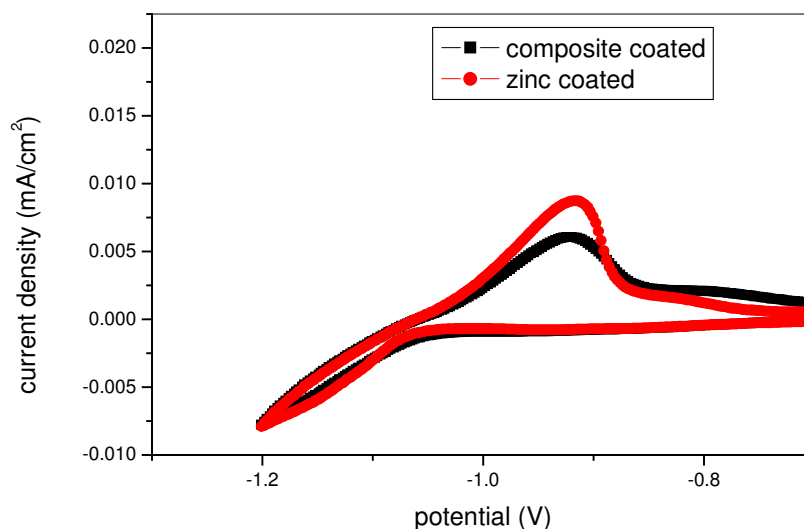

Figure 6. Cyclic voltagrams of bath solution in presence and absence of carbon black Nano particles

The cyclic voltamograms of pure electrolyte and electrolyte containing carbon black particles are shown in Fig. 6. It was evident from cyclic voltamograms that presence of carbon black in the electrolyte reduced the cathodic peak current. It indicated that over voltage was increased for reduction of zinc. Also it was noticed that there was reduction in the anodic peak current and inferred lower rate in the dissolution of zinc of composite coating.

3.4. Microhardness measurements

The microhardness values are shown in Fig. 7. According to Hall-Petch Law microhardness values are increased with decreasing particle size. In this case also in the presence of carbon black the grain size of the coating was reduced, so microhardness values increased. Microhardness values of composite coated sample was 90 against 72 of zinc coating.
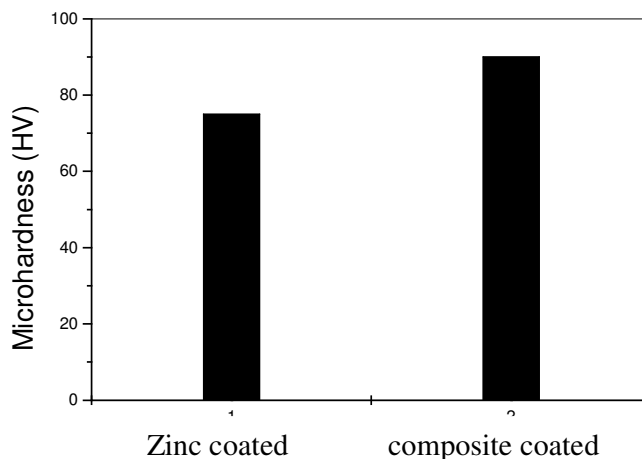

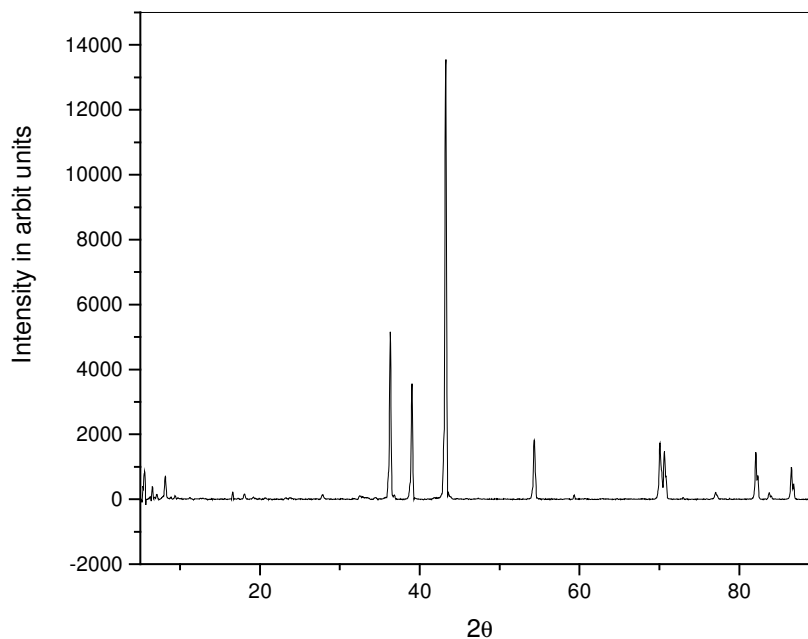**Figure 7.** Microhardness values of pure zinc and composite coating samples

Figure 8. XRD of composite coated sample.

3.5. Surface morphology

Fig. 8 shows the XRD pattern of the electrodeposited composite coating. The average crystal size of the composite coating was 34 nm. This was also supported by SEM images. During

electrodeposition the crystal size was monitored or guided by the rate of fresh nuclei formation or rate of growth of crystal. Fine grained deposit generally obtained at higher rate of formation of nuclei. The addition of carbon particles may provided large number of cathodic sites and consequently more number of fresh nuclei formed on metal surface. This results in fine grained composite deposit.
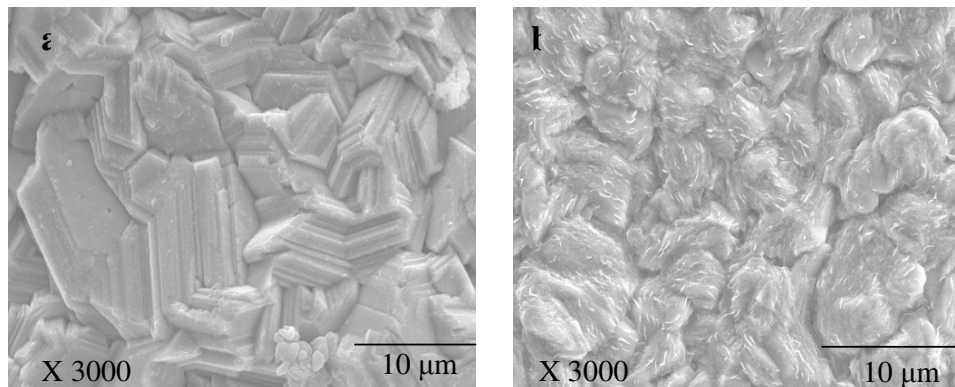

Figure 9. SEM images of pure zinc coating (a) and composite coating sample (b).

Fig. 9(a) and (b) shows the SEM images of pure zinc coated and composite coated samples respectively. The grain size of the composite coated sample was smaller than pure zinc coated sample. In pure zinc coating the crystals of different size were oriented randomly and there was no size uniformity (Fig. 9a). But in composite coated sample more uniform crystals were observed (Fig. 9b)
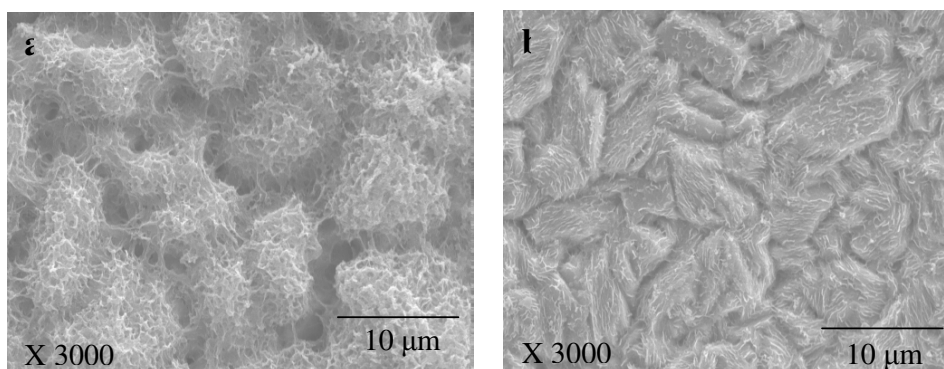

Figure 10. SEM images of pure zinc coating (a) composite coating (b) after 15 weight loss measurments

Fig. 10(a) and (b) shows the SEM images of pure zinc coated and composite coated samples after corrosion experiments. The coated specimens were immersed in 3.5% NaCl for 360 hours. The SEM image of zinc coated sample exhibited the corrosion products (white rust) on the entire surface,

but composite coated sample showed negligible amount of corrosion products. These results inferred that the composite coated sample retained its original surface even after 15 days of immersion in NaCl and posses higher corrosion resistance property.

4. CONCLUSIONS

1. The Zn-carbon black composite was successfully electrodeposited on steel sheets from a zinc electrolyte

2. Chemical and electrochemical corrosion studies of composite showed good corrosion resistance property

3. Corrosion rate was smaller in composite coated sample

4. Salt spray test revealed higher service life for composite than pure zinc coating

5. Microhardness values were slightly higher in composite coated sample

6. XRD studies showed that the crystal size of composite coated sample was 34 nm

7. SEM images indicated the negligible corrosion at the composite coating surface

8. Carbon black showed good reinforcing action

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