Zno Containing Duplex Coating to Galvanized Steel for Corrosion Resistance

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ABSTRACT

Galvanized steels are widely used in applications where high corrosion resistance anticipated. But still it is prone to corrode in a chloride & SO2 containing environment. Thus in order to isolate the component from such an environment and to improve its life paints are applied on galvanized steel. The nanocomposite is prepared by adding ZnO particles in epoxy mastic mechanically & painted on galvanized steel.Corrosion resistance of the composites film was studied by an electrochemical impedance spectroscopy (EIS) in 3.5 % NaCl electrolyte solution & salt spray test.The water ingress capacity of the coating is studied by long term immersion test along with EIS.

Keywords*: Galvanized Steel, Nanocomposite, EIS, Corrosion Resistance. Corrosion Protection Efficiency*

1. INTRODUCTION

Metals and its alloys corrodesin an environments encountered during their service. Corrosion can be defined as the destruction or deterioration of a material because of reaction with its environment [1]. Corrosion can be initiatedby chemical or electrochemical reaction with the surrounding environment. The most common examples of corrosionprocess arediscoloration, rustingand tarnishing [2].Corrosion ofmaterialis disease, it cannotbe prevented completely, and itcan only bereduced or delayedbecause thermodynamically it is a spontaneous phenomenon.. Corrosion ofmaterialis disease, it cannotbe prevented completely, and itcan only bereduced or delayedbecause thermodynamically it is a spontaneous phenomenon.

1.1 Coatings

Several types of organic and inorganic coatings are applied over the finished metal surfaces. These coatings applied on metal substrate for decorative or functional purpose and/or combination of the both.Functional coatings severed as corrosion resistant or wear resistant or of combination of both[3]. Organic coatingare epoxy base binder mainly used for low temperature applications i.e. for corrosion resistancewhile the inorganic coatings are silicates base binder used for high temperature, corrosion resistance or wear resistance or combination of both[4].

1.2 Galvanised steel

Galvanising is a one of the approachto give cathodic protection tocarbon steel for superior corrosion resistance and excellent sacrificial protection capability.However due to rising cost of zinc, Zn-Al alloys arebeingused[5]. Some notable Zn-Al commercial alloys are Galvalume, Galfan, ZAM&Superdymaas shown in table 1.Galvanised steel used in Automotive, power transmission lines, Automotive, power transmission lines, Telecommunication industries,thermal power station, andmany more applications[6].

Type	Metal Coating	Alloy Composition, % by Weight				
A	Zinc Coating	0.2	0.3			99.5
B	Galvalume	55	-	1.6		43.4
C	Galfan	5	-		0.12	94.4
D	ZAM	6	-		3	91.0
E	SuperDyma	11	-	0.2	3	85.8

Table 1 Chemical compositionsofhot dipped commercialzinc alloy coatings [7]

1.3 Corrosion in galvanised steel

Becauseof its negative standard redox potential (-0.76 V/SHE),Zn is very active metal and tends to corrode in contact with oxygenand moisture [8].Zinc galvanised steel is sensitive to the severe and harsh environment such as SO2and chlorine contamination.steel. It takes 6 monthsto2 yearsperiod to develop fullyweathered galvanized steel.The zinc carbonate film is very stable& good paint adhesion properties than partially weathered galvanised steel, attributed to the less solubility& finely etched surface.

1.4 Duplex coating

The combination of a paint system with a hot-dip galvanized coating is often referred to as a “duplex system”. Hot-dip galvanized steel parts or assemblies are often required to be painted. The reason for painting can be to identify the particular structure, for architectural purposes, to provide a particular type of protection, or to extend theservice life of an existing structure. [9]. When paint and galvanized steelduplex system is used, the corrosion protectionobtained is superior than obtained by an individual system[9]. This combination of coatings delivers superior cathodic protection from the galvanizing and some barrier protection from the Zinc carbonate patina & superfluous barrier protection by coating.

2. Corrosion Study

Electrochemical studies will be carried out using open circuit potential measurements, Tafel analysis, impedance spectroscopy and alternate immersion testing. The electrochemical cell is coupled with potentiostat /galvanostat (Gamry Reference system 600, ZRA System, Wilmington, USA) for these measurements[10].

2.1 Tafel Polarization

Tafel extrapolation method will be used to determine corrosion rate of the paint coated sample. In this technique, the polarization curves are obtained by applying potential of ± 250 mV with respect to open circuit potential. Resulting Tafel plots contain anodic and cathodic branches. Plotting the logarithms of Current vs. Potential and extrapolating the current in the two Tafel regions gives the corrosion potential and the corrosion current. By using curve fitting corrosion current density, corrosion potential & corrosion rate can be determined[11].

2.2 Electrochemical impedance spectroscopy:

EIS have been emerged as an important tool for studying corrosion of metals and alloys. Electrochemical impedance spectroscopy, a method designed to avoid severe deterioration of the exposed surface of the structure studied, consists of applying frequencies and low amplitude sinusoidal voltage wave to produce perturbation signals on the electrode

Parameters	Values
Initial Frequency Khz	100
Final Frequency	0.01 Hz
Points/Decade	10
A.C Voltage	10 mV
D.C Voltage	0 V
Initial delay	50 Sec
Method	Potentiostatic

Table 2EIS parameters used for test.

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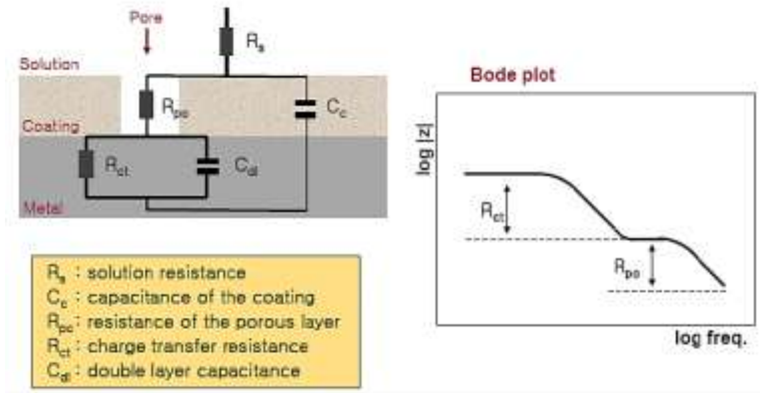

Figure 1 – Equivalent electrical circuit and resulting Bode plot.

These plots are, subsequently, to be modeled using equivalent circuits and quantitative information as well as mechanistic information about coating performance can be obtained.

2.3 Alternating immersion testing:

In order to access the performance of the coated samples under drying and wetting cycles in atmosphere, the coated samples were tested for alternating immersion test. The coated sample is suspended from the spokes of the wheel (300 mm diameter) by a thread so that there is no metallic contact between the two. The speed of rotation of wheel is to be kept constant 0.2 rpm so that each rotation can be completed within 5 minutes. During each rotation, the sample gets partially immersed in 3.5 wt. % NaCl aqueous solution andexposed to atmosphere. The performance of the coated samples was studied under drying and wetting cycles in atmosphere. The potential is measured with the help of multimeter against SCE after 24 hours duration.

2.4 Salt spray test

Salt spray test is carried out to check the corrosion resistance of the coating exposed to the 5% NaCl fog. The cut edges of the specimen are sealed with araldite to avoid corrosion at the edges. Exposure test in the salt spray cabinet system (Swiss Engineers Pune) are carried out according to the ASTM B117 [12]. For testing purpose 5% NaCl solution is used. The exposure zone of the salt chamber is maintained at 35+ 1°C. The coated samples are exposed with salt spray until the first red spot is observed on the exposed specimen.

3 Result and Discussion

3.1 The potentiodynamic polarization

The Tafel polarization test carried out on different composition of nanocomposite coating (1-10 % ZnO) on Gamry instrument (Reference 600). Stainless steel plate is used as a counter electrode, standard calomel electrode as reference electrode & 3.5% NaCl solution as electrolyte. Tafel curve (potential vs. current density) obtained from the experiment for 0.5% Zno in figures 2.

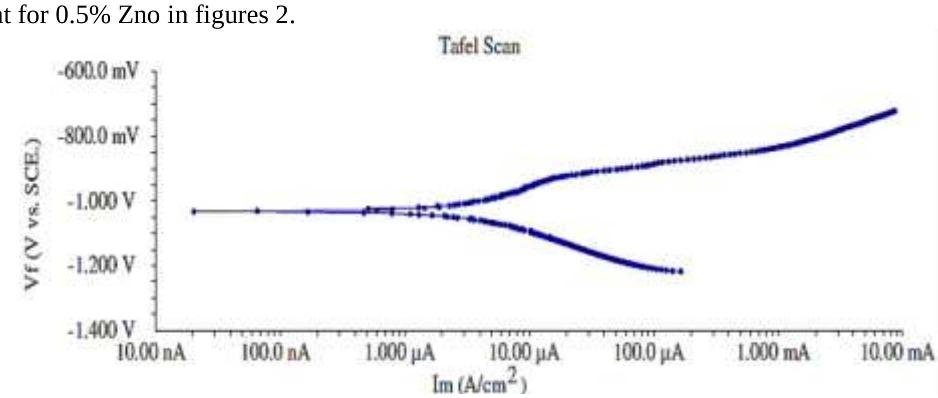

Figure 2 Tafel plot for sample coated with 0.5% ZnOnanocomposite in 3.5 wt.% NaCl.

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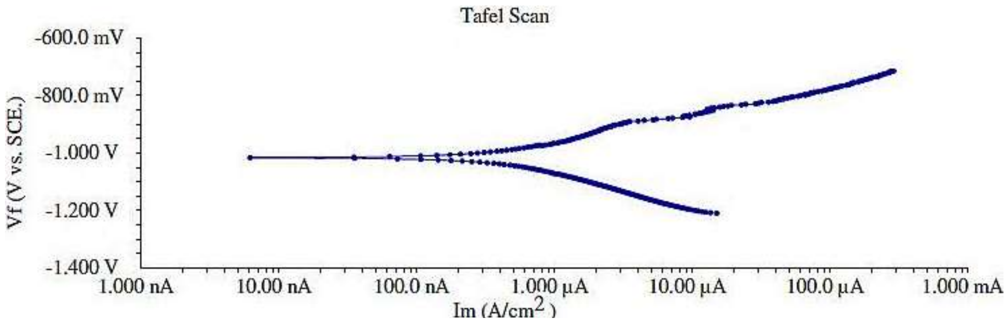

Figure 3 Tafel plot for sample coated with 1% ZnOnanocomposite in 3.5 wt. % NaCl.

Sample	**Ecorr(mV)**	**Icorr (A/cm2) nA**	**Corrosion rate mpy**
Galvanized	-616.0	2450	1.8181
0.5 % ZnO	-1030	1510	0.6143
1 % ZnO	-1020	779.0	0.3171

Table 3 Corrosion rates for different weight compositions of ZnO in nano composite

3.2 Corrosion protection efficiency

Corrosion protection efficiency with change in content of ZnO in nanocomposite coated on galvanized steel is calculated by using an equation [13].

$$\textbf{PE \%} = \frac{Rp-(Uncoated)-Rp^{-}\ Coated}{Rp-(Unocated)} \times \mathbf{100} \ldots\ldots\ldots\ldots\ldots\ldots\mathbf{1}$$

Polarization resistance Rp obtained from EIS for uncoated sample is 322.2. The polarization resistances for different weight composition were obtained from CPE curve fitting of Nyquist plot.The variation of the corrosion protection efficiency as a function of ZnO composition in the coating.Polarization resistance Rp obtained from EIS for uncoated sample is 322.2 ohm. The polarization resistances for different weight composition were obtained from CPE curve fitting of Nyquist plot. The protection efficiency of nanocomposites coated on galvanized samples with different weight fraction of ZnO in nanocomposite is tabulated in table 5.6 by using above equation 1.

Sample (Wt. %)	**Rp (ohms)**	**Protection efficiency (%)**
0.5 % ZnO	3.883e3	91.70
1 % ZnO	31.40e3	98.97

Table 4 Protection efficiency for different compositions of ZnO.

5.10 Alternate immersion testing:

Alternate immersion testing is carried as per ASTM-G44-99 [14]. The potential was measured at the water air interface on coating for every 48 hours. Table 5.14 shows change in potential with time for two samples of same composition (0.5% ZnO) and a graph of potential as a function of time is shown in figure 4& figure 5

Time (hrs.)	**Potential Sample 1 (V)**	**Potential Sample 2 (V)**
0	0	0
48	-0.232	-0.245
96	-0.243	-0.254
144	-0.253	-0.277
192	-0.254	-0.284
240	-0.265	-0.282
288	-0.253	-0.278
336	-0.277	-0.275
384	-0.305	-0.307
432	-0.332	-0.32
480	-0.29	-0.326
528	-0.317	-0.32

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Table 5 Potential values for intact sample for different immersion time in 3.5 % NaCl.

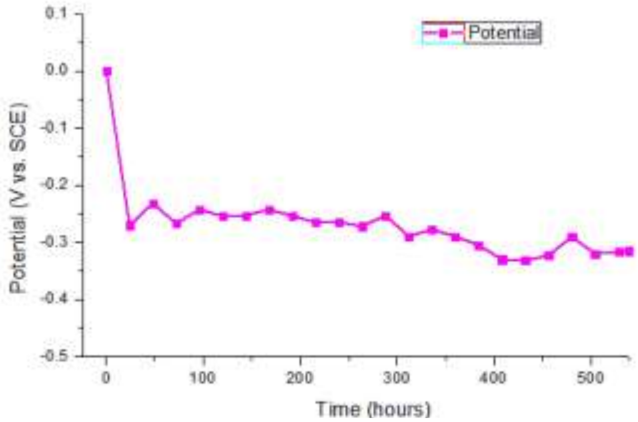

Figure 4 Potential as a function of time, for Sample-1 (5% ZnO) nano composite coating coating.

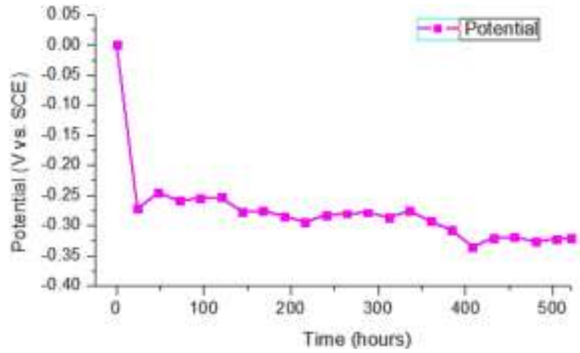

Figure 5 Potential as a function of time, for Sample-2 (5% ZnO) nano composite

The results reveal that the potential is decreasing uniformly & become more & more negative, the graph shows cathodic shift.

5.14 Salt Spray test:

Salt spray test measures the ability of coatings to withstand in accelerated corrosive cum humid environment. The tests were conducted as per ASTM B-117 [15]. The samples are introduced in a salt fog spray chamber.

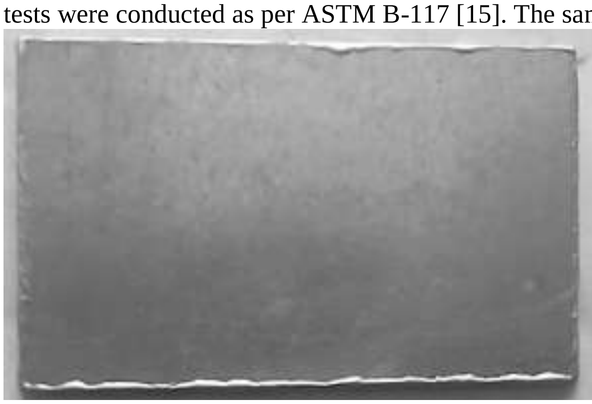

Figure 6: Photograph of salt spray test galvanized sample after 0 hours

Figure 7 : Photograph of salt spray test Galvanised steel after 1200 hours.

Figure 8: Salt spray test sample nano composite(0.5% ZnO) coated sample after 0 hours.

Figure 9: Salt spray test sample nano composite (0.5% ZnO) coated sample after 1200 hrs.

The photographs are taken at 0 hrs. as shown in figure 6& figure 7. Samples are then exposed to salt spray test for 1200 hrs. of exposure and photographs are taken as shown in figure 8 to figure 9. Form the visual inspection of nanocomposite coated sample there is deterioration of the coating is observed, no red rust, no white rust & no blister formed after 1200 hrs. of exposure.

Conclusions

The corrosion resistance of ZnOnanocomposite on galvanized steel, immersed in 3.5% NaCl solution was studied by electrochemical spectroscopy impedance (EIS) & potentiodynamic polarization techniquesProtection efficiency is high for 0.5 wt. % coating due to uniform distribution of nanoZnO particles, no agglomerates & free from micro porosity.A coated sample exposed to a salt spray test shows no deterioration of the coating after 1200 hours of exposure, whereas the galvanised sample exposed along with coated sample shows formation of red rust at 720 hrs. at some localised region on the galvanized steel.

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