Fishery Technology 57 (2020) : 101 - 107

Nano zinc – titanium – cerium Coating on BIS 2062 Boat building Carbon steel for Corrosion Protection

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Abstract

The corrosion inhibition ability of three nano oxides, zinc oxide, titanium oxide and cerium oxide coating over BIS 2062 carbon steel was studied. Morphology of the coating evaluated using SEM and AFM techniques and it showed uniform coverage over the surface and lower roughness than untreated steel. Electrochemical measurement in 3.5% NaCl showed 3.5-fold increase in polarization resistance than bare steel. The electrochemical impedance spectroscopy data was exhibited comparable results as that of linear polarization studies. The nano xode mixture having 0.01% each of zinc and titanium and 0.02% cerium showed adequate corrosion protection under the marine environment.

Keywords: marine corrosion; nano metal oxide; corrosion protection; electrochemistry

Introduction

Construction of steel fishing boats and canoes were mainly carried out by using BIS 2062 grade steel. The material undergoes corrosion in marine environment when the coating fails to render protection during friction between the boats docked in the harbour. Hence it is essential to develop a coating which is resistant to scratches and friction. Studies on barrier protection of metals were carried out by applying pure organic or inorganic-organic composite materials. The efficiency of protection depends on the environment and barrier properties. Recent studies showed that nano material incorporated organic layers are used for barrier protection (Dhokea et al., 2009, Kumar et al., 2009; Rosu et al., 2009). Application of nanomaterials as coating provides transparent or semitransparent coating due to their small size and non-migratory character. Nano-sized oxides of titanium, zinc, iron, and cerium are well known cathodic inhibitors and UV absorbers with a high refractive index. Zinc oxide is known for its non-toxic characteristics, non-migratory nature, biocompatibility, increased electronic conductivity, electron transfer ability, protein bio mimic behavior, photo catalyst and safety of use (Fangli et al., 2003; Popa et al., 2006; Yang et al., 2005; Montazer & Amiri 2014; Zhu et al. 2007; Joshy & Khader 2001; Zhang et al. 2004). Nano zinc oxide is a wide gap n type semiconductor with an optical band gap in the ultraviolet region (Anz¡lovar et al., 2010; Zhu et al., 2007). Electroless nickel plates (EN) incorporated with nano oxides of zinc improved the metallurgical and corrosion resistance characteristics (Shibli et al., 2006; Rashvand et al., 2012). The addition of metal oxide along with nano zinc oxide in a phosphate-bath improved microstructure of the coating and increased corrosion resistance (Akhtar et al., 2006; 2007). Titanium phosphate was used as a precursor to activate zinc phosphating on steel (Wolpers & Angeli, 2001). Nano titanium oxide and nano cerium oxide are already proven cathodic inhibitors, and their characteristics are mentioned elsewhere (Ashraf & Edwin, 2013). A recent study by Ashraf & Anuradha (2018) showed the mixtures of nano iron, titanium, and cerium oxide coating over 2062 steel showed excellent corrosion resistance under marine environment. In the above works of literature, it is clear that nano cerium oxide, titanium oxide, and zinc oxide have their own roles in the corrosion protection in steels. An optimum ratio of these materials in a mixture can play an important role in corrosion resistance, healing effect, and microbial attack. Not many studies have been carried out to determine the efficacy of multifunctional oxide mixtures as a coating material to protect steel from corrosion. Application of nano-sized material coating over

Received 11 December 2019; Revised 18 March 2020; Accepted 20 March 2020

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steel is expected to have higher coverage, increased cathodic inhibition, low coating failure, and transparent. The present study aims to prepare a nanocoating comprising of nano oxides of zinc, cerium, and titanium mixture over boatbuilding steel and to understand its electrochemical characteristics in marine environments.

Materials and Methods

Nanomaterials, nano zinc oxide (average size 14 nm, Specific surface area: 30±5 m^2g^{-1} Purity: > 99%), titanium oxide (4-8 nm anatase phase and nitric acid stabilized) were procured from Reinste Nano Ventures India Private Limited, New Delhi. Nano cerium oxide was prepared as described by Fu et al. (2005) and its size was about 30-40 nm by AFM studies. The BIS 2062 grade B carbon steel was purchased from Government run Kerala State Inland Navigation Corporation (KINCO), Cochin, and its chemical composition was carbon 0.22%, manganese 1.5%, silicon 0.4%, phosphorous 0.045%, sulphur 0.045% and rest is iron. All other laboratory chemicals were purchased from Merck India, and used as received.

The steel coupon having size 3×5 cm was cleaned by pickling in 5% H_2SO_4 for 3 min preceded by washing with MilliQ type 1 water and dried in air. The steel sample surface was polished up to 1000 grits using 300 to 1000 grits SiC papers. Coupons were sonicated in acetone for 30 min and repeated the process with water. The dry coupons were kept in a desiccator till analysis. The nano mixture solutions of varied concentrations were prepared by dispersing in dimethyl formamide and their concentrations showed in Table 1. The suspensions were sonicated for 1 h and the nano mixture solution coated over the steel coupon at the rate of 40 ml m^{-2} area. The coating carried out in all the sides of the specimen. The coupons were stored at 100 °C in an oven for 1h.

Electrochemical evaluation of the steel was done using Metrohm PGSTAT 302N with FRA2 electrochemical workstation using a standard three-electrode system with Ag/AgCl (3M KCl), Pt and steel as a reference, counter, and working electrode respectively. NaCl solution (3.5%) was used as the electrolyte. Linear sweep voltammetric analysis was done with a potential scan rate of $0.001Vs^{-1}$ after 1 h exposure in the electrolyte. Tafel plots were analyzed using Metrohm's Nova software. Electrochemical impedance analysis (EIS) was carried out at open circuit potential and the frequency scanned from 100 KHz to 0.1 Hz in 50 decades after half an hour immersion in the electrolyte. The resultant EIS data was derived after fitted with simple Randle's equivalent circuit model. The experiment was repeated three times in all the cases, and the mean data was used for comparison.

Corrosion rate was evaluated by weight loss method as per ASTM G1. Pre weighed coupons were exposed for 40 days in 3.5% NaCl solution, retrieved, cleaned by sonication, washed with Milli Q water, dried at 100 °C for half an hour in an air oven and allowed to cool in a desiccator. Corrosion rate was evaluated using the formula,

Corrosion rate CR = 534W/DAT, ………………… 1

where, D is density, W is the weight loss, A area in square inch and t time in hours.

Steel coupons having 0.5 cm^2 area was polished upto 2000 grit by using a series of SiC papers. Degreased by sonication in acetone and then in water. Nanomaterials were coated as per the treatment details described above. AFM topographical measurement was done under non-contact mode

Table 1. Treatment details of nano zinc oxide, cerium oxide and titanium oxide coated steel.

Treatment	Nano ZnO %	Nano CeO_2 %	Nano TiO_2 %
Z0	0	0	0
Z1	0.01	0	0.01
Z2	0.01	0.01	0
Z3	0.01	0.01	0.01
Z4	0.02	0.02	0.02
Z5	0.01	0.02	0.01
Z6	0.02	0.02	0.01

by using Park XE 100 AFM with XEI image processor. The Si scanning probe with < 10 nm tip was used for scanning the surface. The microstructure of the steel coupon was studied using JEOL JSM - 6390LV Scanning Electron Microscope.

Results and Discussion

Scanning electron micrographs of nano zinc oxide – titanium oxide-cerium oxide (ZTC) mixture coated steel was shown in Fig. 1. Flakes of nano ZTC was formed over the steel uniformly, and in the interstitial spaces the ZTC particles were strongly bonded with steel. ZTC coating over the steel increased the particle coverage and reduced the grain size. Nano ZTC covered the surface of the steel, which activated the nano sized cathodic sites on the surface (Shibli & Chacko, 2011; Zhang, 2009; Sheng et al., 2011). The more the nano ZTC content, the more flake like structure was seen over the surface.

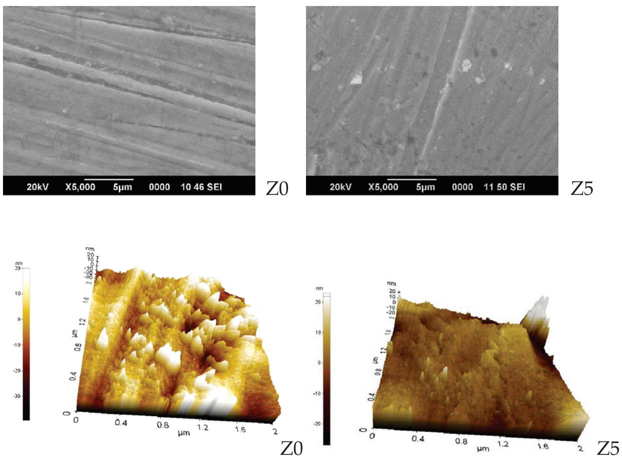


Fig. 1. SEM and AFM topographs of nano zinc oxide, cerium oxide and titanium oxide coated boat building steel

The surface AFM topographic images of ZTC coated steel samples are shown in Fig 1. The results showed that the nano oxides fully covered the grain boundaries and were uniformly distributed. Nanomaterials are known for their ability to have higher surface area coverage and adhesiveness (Voevodin et al., 2003; Bjerklie, 2005). Roughness, average surface roughness (Ra) and root mean square roughness (Rq), of the surfaces were evaluated (not shown in Figure). The Ra values were 5.23, 2.00, 1.39 and 1.92 nm for Z0, Z1, Z2, and Z5, respectively. Similarly, Rq values were 6.50, 2.41, 1.87 and 2.33 nm respectively for Z0, Z1, Z2 and Z5. The order of roughness was Z2 < Z5 < Z1 < Z0. Nano zinc oxide – cerium oxide mixture coated surface showed comparatively lower roughness. The introduction of nano titanium oxide along with nano zinc and cerium oxide showed an increase in the roughness (Z5). Nanomaterial coated surface showed significant reduction in roughness than untreated control. The nano-particles were filled in the grain boundaries of the steel matrix. This may lead to the sealing of anodic sites and the resultant reduction in the corrosion rate.

Linear sweep voltammetric analysis data of the ZTC coated steel was shown in Fig. 2 and the Tafel slopes were shown as Fig. 3. Corrosion potential (Ecorr), corrosion current density (Icorr) and polarization resistance (Rp), varied from -0.829±0.016 to -0.699±0.041 V, $1.74\times10^{-5} \pm 1.35\times10^{-5}$ to $1.21 \times10^{-4} \pm1.03\times10^{-4}$ Acm^{-2} and 542±29 to 2966±453 &!cm^2, respectively. The highest Rp and lowest Icorr were exhibited by the treatment Z5. The Ecorr of untreated coupon showed higher standard deviation. The Ecorr values of bare steel exposed to 3.5% NaCl was lowest compared to the treated samples. The Ecorr values of all ZTC coated specimens were higher than bare steel except in Z1. The increased corrosion resistance of Z5 implied the enhanced porosity, improved coverage and uniform coating over the steel. Two metal oxide coated samples, Z1 (nano zinc and cerium oxide coating) and Z2 (nano zinc and titanium oxide coating), exhibited increased Rp and Icorr. When CeO_2 was included along with ZnO and TiO_2 the Rp values were decreased. This was further decreased in Z4 due to the doubled quantities of nano oxides. The result shows that there was an antagonistic effect, between the particles or number of particles in square area. Variable ratios of nano material applied in Z5 showed significant increase and decrease respectively in Rp and Icorr. Z5 exhibited very effective corrosion resistance evidenced by Rp and Icorr values. Because of the barrier effect of the nano ZTC coating, there was a significant decrease in Icorr and increased Rp were showed in Z5 than untreated control. Z5 exhibited seven fold lower Icorr and 3.5 times higher Rp values. Here the TiO_2 and ZnO were half the amount of CeO_2. This shows synergestic influence of CeO_2 and ZnO-TiO_2 ratios. The protection efficiency was calculated based on the formula

Protection efficiency $P = (R0-Rp)\times100/Rp$ …………2

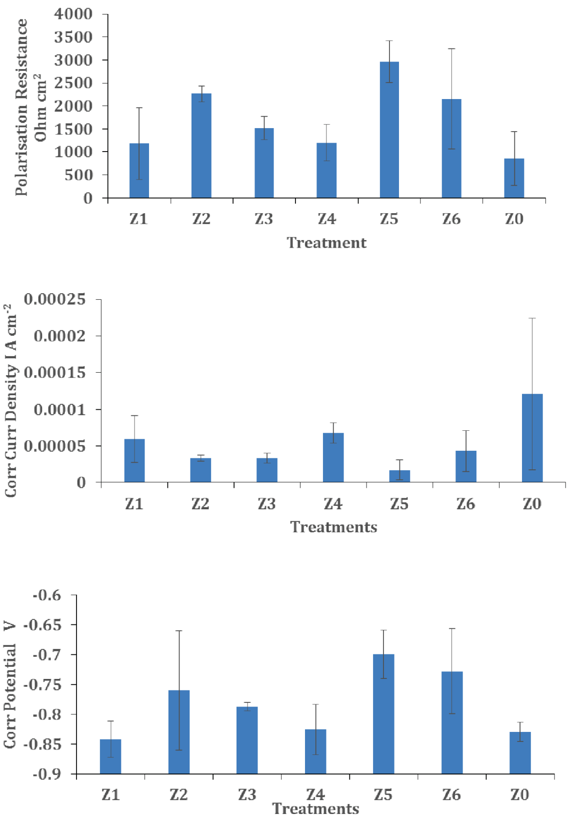
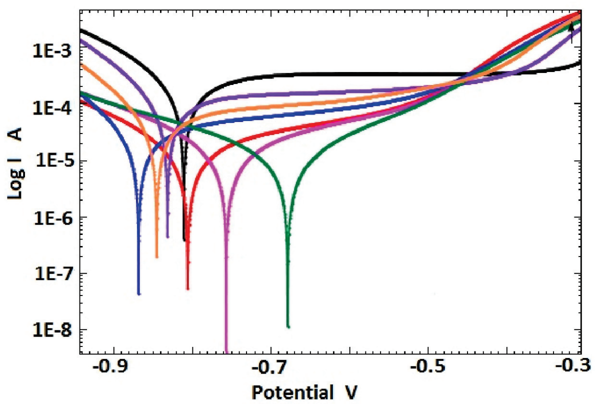


Fig. 2. Linear sweep voltammetric data of nano zinc oxide, cerium oxide, and titanium oxide coated boatbuilding steel



Z0 black, Z1, blue, Z2 red Z3 violet, Z4 brown Z5 green, Z6 pink

Fig. 3. Tafel's slopes of nano Zinc oxide-Cerium oxide-Titanium oxide coated steel

The protection efficiency due to the treatment was 71% higher than bare steel.

In Z5, the TiO_2 and ZnO concentration were half of cerium oxide and this probably had influenced higher corrosion resistance. Similar trend was showed in cerium oxide – titanium oxide incorporated aluminium, where 2:1 ratio of CeO_2: TiO_2 showed excellent corrosion resistance (Ashraf & Edwin, 2013). Nano ZnO and CeO_2 contribute by increasing the cathodic sites and TiO_2 enhances the production of hydrogen peroxide. All the three helped to seal the anodic sites thereby reduced anodic reaction. This shows that ZTC protected the steel from aggressive corrosive environments. Similar behaviour was exhibited when nano zinc oxide was incorporated in a phosphating bath (Tamilselvi et al., 2015; Arthanareeswari et al., 2012). The nano sized crystals of ZTC exhibited higher coverage and improved coating efficiency (Shibli & Chacko, 2011; Minqi et al., 2011). The corrosion current density decreased significantly in ZTC coated steel surface which shows that the surface was more uniform and less porous. The optimum ZTC ratio in the mixture favoured better surface coverage and homogenous coating, which led to the decrease of corrosion resistance of the steel substrate. ZTC at Z5 enhanced compact nucleation and denser morphology containing more cathodic and toxic sites (Tamilselvi et al., 2015). The behaviour of surface and internal layers of the matrix would be better highlighted by the EIS data.

Electrochemical impedance spectral data of ZTC steel are shown in Fig 4. The data obtained was analyzed by fitting it with simple Randle's equivalent circuit model (Rs [R1C1(R2C2)]). Where Rs is the solution resistance between the working and reference electrodes, R1 and R2 are charge transfer resistances in the high and low frequency domains respectively. Constant phase element (CPE) was used in lieu of simple capacitor (C). C1 and C2 represent the CPE in the high and low frequency domains. Fitted Bode plots are illustrated as Fig 5. The Nyquist plot had two well developed sections, one in high frequency region and one in low frequency domain. HF domain represents the outer most coating layer of ZTC and the second, low frequency domain, represents the internal layer of the boat building steel. HF domain polarization resistance and constant phase elements varied from 36.3 ± 3.9 to 256.5 ± 71.4 Ohm cm^2 and $1.69 \times 10^{-09} \pm 1.21 \times 10^{-10}$ to $1.65 \times 10^{-8} \pm 2.25 \times 10^{-9}$ F respectively. Where as in the LF domain, the Rp and CPE respectively ranged from 98.0± 33.1 to 345.0±42.0 and $7.80 \times 10^{-4} \pm 2.61 \times 10^{-4}$ to $6.35 \times 10^{-3} \pm 9.54 \times 10^{-4}$ F.

Highest Rp was exhibited by the coupon treated with 0.01% ZnO, 0.02% CeO_2 and 0.01% TiO_2. The results interrelated with the findings of the LSV studies.

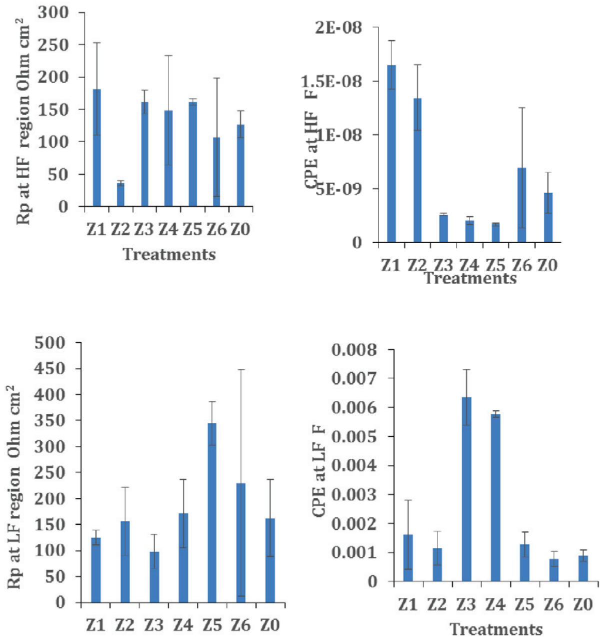
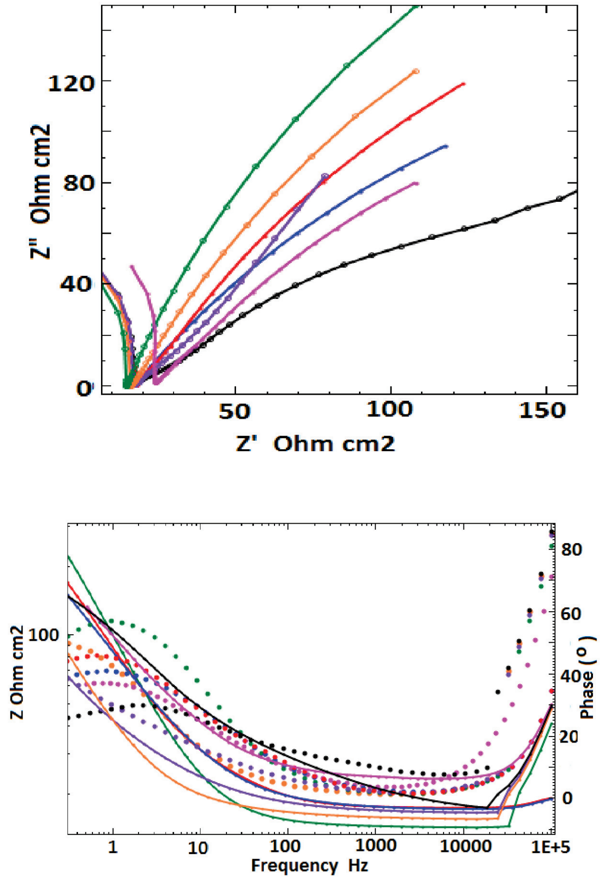


Fig. 4. EIS data of nano zinc oxide, cerium oxide and titanium oxide coated boat building steel.

The Nyquist plots were almost identical in all the cases but the Z5 exhibited wider diameter (Fig 5). On close examination at the interface between the HF and LF domain regions (Fig 6) showed a significant difference in the closeness between the treatments. Z0, Z1, Z2, Z3, Z4, Z5 and Z6 showed angles 55, 37, 29, 50, 35, 22, and 43° respectively. Among the treatments Z5 showed the lowest angle and the highest angle was for Z0, bare steel. This shows the ZTC layer in Z5 had very close interaction or association between the internal layers of the boat building steel. This led to a higher corrosion resistance in Z5. Whereas in the bare steel, the native iron oxide layer existed as an independent entity, evidenced by Nyquist plot with wider gaps between HF and LF domains indicating the lowest association with the internal layers of the steel. Also, the iron oxide layer had become more porous which allowed to interact the electrolytes with internal layers. The ZTC treatment reduced the gap or increased the interaction between the outer layer and internal layer and decreased the porosity over the matrix which favored the corrosion inhibition. The EIS results showed the corrosion behaviour of ZTC treated boat building steel was more diffusion controlled and this favoured increased corrosion resistance.



Z0 black, Z1, blue, Z2 red Z3 violet, Z4 brown Z5 green, Z6 pink

Fig. 5. Bode and Nyquist plots of nano Zincoxide-Cerium oxide- Titanium oxide coated steel.

The results showed that the ZTC coating over boat building steel formed non porous and active surface than bare steel. The anodic reaction in the bare steel increases the release of the iron oxide to the electrolyte and the cathodic reaction depolarizes the dissolved oxygen. This leads to the acidification and hydrolysis of the Fe ions (Girèienë et al., 2013). This enhances the penetration of aggressive electrolytes and leads to corrosion on the surface. Treatment of ZTC over steel surface created less porous surface with best protecting abilities. Nano cerium oxide and zinc oxide act as cathodic inhibitors and the titanium oxide favors formation of acidic surface which deters the growth of microorganisms responsible for biocorrosion.

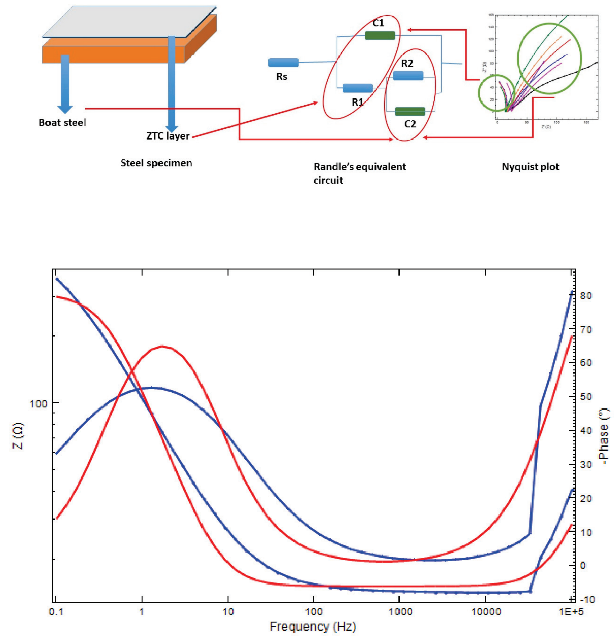


Fig. 6. Randle's equivalent circuit model and its characteristics based on Nyquist plot. Randles equivalent circuit fitted Bode plot of Z6. Bode plots with blue lines shows the actual and red line as fitted plots.

Corrosion rates of ZTC treated boat building steel were measured by exposing the steel coupon into 3.5% NaCl for 40 days (Fig 7). The results showed that the corrosion rates were lowest for Z5. The results were in agreement with linear sweep voltammetry and EIS studies.

Boat building steel BIS 2062 was coated with varied concentrations of nano zinc oxide, cerium oxide and titanium oxide. Surface morphological evaluation exhibited uniform distribution of nano material and improved surface roughness. Linear sweep voltammetric studies showed that treatment with 0.01% each of nano zinc oxide and titanium oxide and 0.02% nano cerium oxide showed highest polarization resistance, lowest corrosion current density and better porosity. Electrochemical impedance data evaluated after fitting with Randle's equivalent circuit showed similar trend as in the linear sweep voltammetric studies. The coating over steel has exhibited effective association with internal layers of the steel as evidenced by Nyquist plots. The paper highlighted the Nyquist plot HF and LF domain characteristics of an efficient system. Corrosion rates determined by weight loss method also exhibited the lowest corrosion rate in Z5 treatment.

The results highlight potential applications of multifunctional nano materials, nano oxides of zinc, cerium and titanium, for effective improvement of corrosion resistance of boat building steel.

Acknowledgements

Authors thank the Director, ICAR - CIFT for the encouragement received to carry out the research. Also thanks are due to the technical and supporting staff of the Fishing Technology Division, ICAR – CIFT.

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