Study of corrosion behaviour of Al$_2$O$_3$ - 13 % TiO$_2$ and Cr$_2$O$_3$ coated ship hull steel in 3.5% NaCl solution

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Abstract: Corrosion degradation of ship hull plates is an important aspect responsible for failure of ships in marine environment. Surface coatings are being used to protect the metallic materials from corrosion. In this work, Al$_2$O$_3$ - 13 % TiO$_2$ coating and Cr$_2$O$_3$ coating were deposited on ship hull building material using D-gun flame spray method. The corrosion behaviour of coatings and substrate was investigated using cyclic polarization test. The microstructure and phase composition of coatings were analysed by scanning electron microscopy (SEM) and electron dispersive spectrum (EDS). The corrosion rate was evaluated from the corrosion parameters extracted from graphs. The uncoated and coated substrates were compared on the basis of corrosion parameters.

Keywords: Cyclic Voltammetry; Corrosion rate; Flame spray; Potentiodynamic polarization

1. Introduction
The highly corrosive nature of seawater is responsible for degradation of engineering materials used in marine environment [1-2]. The marine environment becomes more aggressive due to low electrical resistivity and high salinity [3]. To protect materials from corrosion and increase their life, different methods like corrosion inhibitor, cathodic protection and surface coatings are being used [4-13]. The most popular technique used to protect materials from harsh corrosive environments is by applying protective coatings onto the materials. The passivity is another property of metals which forms a passive layer and protect metals from atmosphere [14]. The passive oxide layer can be destroyed by mechanical and electrochemical methods by immersing the metals in an environment of aggressive ions. The breakdown of passive film is responsible of crevice corrosion, pitting corrosion and localized corrosion. The cyclic potentiodynamic polarization technique (CPDP) is used to investigate initialization of passivity, breakdown of protective film and evaluation of corrosion rate due to scanning potential [15-16]. The CPDP method is a rapid technique used to measure the degradation and corrosion resistance in short span of time [17-18].The alumina and chromia based coatings are becoming popular in providing protection against corrosion and wear [19-23]. The corrosion behaviour of coatings is evaluated using
various corrosion measuring techniques like salt spray test, Tafel polarization, EIS and weight measurement. The CPDP is another common technique used to investigate the corrosion behaviour. The CPDP technique for corrosion behaviour evaluation uses cyclic polarization. The cyclic voltammograms are the plots drawn between the applied potential and current, the curves recorded investigates the corrosion behaviour. There are various studies reported by many authors using cyclic voltammetry for analysing the corrosion behaviour of materials in aggressive environments [24-26]. In the present study Cr$_2$O$_3$ coating and Al$_2$O$_3$ – 13 % TiO$_2$ coating are deposited on ship hull steel by flame spray method. The novelty of present work is in the selection of alloy coating powders, coating deposition method, and the application area [27-28]. Earlier a very little work has been done in this direction as such coatings were mostly used for protecting the components against wear and not for such applications [29-30]. The corrosion behaviour of coated specimen and the substrate are investigated by polarization method. The cyclic voltammograms are plotted between applied potential and current. The corrosion current density, corrosion potential and polarization slopes are extracted from the potentiodynamic curves through Tafel extrapolation techniques. The corrosion rates of substrate, Cr$_2$O$_3$ coating and Al$_2$O$_3$ – 13 % TiO$_2$ coating are compared in this study.

2. Experimental Procedure

2.1. Base Material and Sample Preparation
The material of ship hull plate was used as a substrate for this study. The material was procured from the shipbreaking yard where the ships are dismantled. The substrate of 30 mm × 30 mm × 5 mm dimensions was prepared by vertical milling machine and emery paper of 220, 320, 400, 600, 800, 1000, 1500, 2000 SiC grades were used for grinding the sample to remove surface impurities and provide better adhesion between coating and substrate [31]. After grinding, ABR24 grade alumina grits were shot blasted to remove the even surface, then samples were rinsed with ethanol and were dried immediately before applying coating. The Optical Emission Spectrometer (ATOM COMP 81 Direct Reading Spectrometer with relative humidity 40-60% and temperature range 19 - 25 °C) at CITCO-IDFC testing laboratory, Chandigarh according to IS 8811: 1998 standard was used to determine the composition of ship hull steel. The chemical composition of substrate material is reported in table 1.

| Elements | C (Weight %) | Mn | P | S | Si | Fe |
|----------|--------------|----|---|---|----|----|
|          | 0.2198       | 0.5466 | 0.01960 | 0.01832 | 0.2269 | Balance |

2.2. Coating Powders and Coating Deposition
Al$_2$O$_3$ – 13 % TiO$_2$ (87/13) and Cr$_2$O$_3$ were selected as coating powders because of their good corrosion resistance and adhesion properties after a thorough literature survey [32-33]. The Al$_2$O$_3$ – 13% TiO$_2$ coating powder is composed of 87% Al$_2$O$_3$ and 13% TiO$_2$ with particle size of 45/10 micron. Cr$_2$O$_3$ coating powder (AMPERIT 707 from H.C. Starck, Germany) has particle size of 45/10 µm. The coatings were deposited on substrate using flame spray method in SVX Powder Surface Engineering Pvt. Ltd., Greater Noida, India. The process parameters of spraying are described in table 2. The optimized parameters like spray distance, coating thickness were used throughout the coating process after thorough review [31], [34]. The flow rate of oxygen, acetylene and nitrogen was measured in standard litre per hour (SLPH).
### Table 2: Spray parameters of D-Gun for Al$_2$O$_3$ – 13 % TiO$_2$ and Cr$_2$O$_3$ powder [31], [34]

| Parameter                | Al$_2$O$_3$-13 % TiO$_2$ | Cr$_2$O$_3$ |
|--------------------------|--------------------------|-------------|
| Oxygen (O2) Flow rate LPH| 55 SLPH                  | 50 SLPH     |
| Acetylene (C2H2) Flow rate LPH | 45 SLPH              | 60 SLPH     |
| Nitrogen (N2) Flow rate LPH | 10 SLPH              | 10 SLPH     |
| Spray Distance mm        | 175                      | 175         |
| Coating Thickness µm     | 200-250                  | 200-250     |

#### 2.3. Surface Characterization of Coatings

The JEOL, JSM-IT500 series microscope equipped with Energy Dispersive Spectrometry (EDS) at a typical energy of 20.0 kV was used to perform Scanning Electron Microscopy (SEM) investigations. The seamless data was generated using SMILE VIEW™ Lab, an integrated data management software which links SEM images and EDS analysis results. The porosity of as coated samples was analysed using ImageJ software (using ASTM E2109-01).

#### 2.4. Electrochemical Measurements

The electrochemical tests were performed to investigate the corrosion behaviour of bare and as coated samples in 3.5 % NaCl environment at room temperature (25° C ± 1° C) using Metrohm Autolab PGSTAT302N at Central Scientific Instrument Organization, Chandigarh, India provided with Metrohm Autolab Nova software. The 3.5% NaCl environment is the standard composition used in experimental investigation of corrosion behaviour of materials in marine environment as per the testing standard [35-38]. The three- electrode system with silver/silver chloride (Ag/AgCl) as reference electrode, platinum (Pt) as counter electrode and working sample as working electrode was used for measurements.

##### 2.4.1. Potentiodynamic Polarization Studies

The polarization resistance ($R_p$) and the corrosion rate (C.R.) were calculated from the results obtained in polarization tests. The anodic polarization measurements of samples were performed at 1mV/s scan rate and a potential range from -0.4 V to +0.8 V vs Ag/AgCl [39]. The measurements for cyclic voltammetry were recorded by sweeping the potential linearly from -0.4 V to a positive direction till the required value is obtained and reversed at the same scan rate to form a loop with a complete cycle. The steady corrosion potential was studied for immersion time period of 2 hours. The polarization curves reproduced the values of corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$) and polarization slopes. The corrosion parameters were extracted from curves using Tafel extrapolation technique.

#### 3. Result and Discussion

##### 3.1. Microstructure of Coatings

The SEM micrographs with Energy Dispersive Spectrum analysis of Al$_2$O$_3$ - 13% TiO$_2$ and Cr$_2$O$_3$ are presented in figure 1. The microstructure is observed in SEM and the composition is analyzed with EDS. The figure 1 (a) represents the microstructure and composition of Al$_2$O$_3$ - 13% TiO$_2$ coating. The micro pores were observed in the microstructure of coating. The micro cracks were not seen in the micrograph. Also columnar grains and laminar microstructure were absent in Al$_2$O$_3$ - 13% TiO$_2$ coating. From earlier studies it has been revealed that the presence of cracks, pores, laminar microstructure and splats is responsible for degradation of materials [40-41]. Figure1 (b) describes the surface morphology and composition of Cr$_2$O$_3$ coating.
Figure 1: Microstructure and EDS analysis of Al₂O₃ – 13 % TiO₂ coating and Cr₂O₃ coating: (a) SEM micrograph Al₂O₃ – 13 % TiO₂ coating, and EDS analysis of Al₂O₃ – 13 % TiO₂ coating, (b) SEM micrograph of Cr₂O₃ coating, and EDS analysis of Cr₂O₃ coating.

The fragmented particles were observed in the micrograph. The coatings deposited by flame spraying method observed dense structure. The average porosities of Al₂O₃ – 13 % TiO₂ and Cr₂O₃ coating were 2.293 % and 1.69 % respectively determined using image analysis. The Cr₂O₃ coating is much denser than Al₂O₃ – 13 % TiO₂ coating.

3.2. Potentiodynamic Polarization Behaviour

The corrosion behaviour of substrate and coated samples was evaluated by potentiodynamic polarization tests and the corresponding results are shown in figure (2-4). The typical cyclic polarization curves were obtained for substrate, Al₂O₃ – 13 % TiO₂ coating and Cr₂O₃ coating in figure (2-4) respectively. The Tafel extrapolation technique was used to analyse the anodic and cathodic slopes [42], corrosion current density (Icorr) and corrosion potential (Ecorr). The corrosion rate was calculated using Eq. 1 [43]. The results are given in table 3.

\[
\text{Corrosion Rate (C.R.)} = \frac{3.17 \times EW \times I_{corr}}{d \times A} \tag{1}
\]

Where EW = equivalent weight (gram/equivalent), d = density (gram/cm³), A = sample area (cm²)
In figure 2 the voltage is applied to the reference electrode through a potentiostat. The sharp increase is observed in the current density. As the potential is applied the dissolution of ions start in the electrolyte and the electrons start flowing from the working sample. The small passive region recorded in the polarization curve indicates the severity of the pitting attack by the chloride ions. The phenomenon of pitting corrosion is also seen when the potential scan is reversed as pitting corrosion is enhanced after formation of pits. The formation of loop in the figure indicates less corrosion resistance of the material. The absorption of negative chloride ions initiates the breakdown of passive film and formation of pits [44].

Figure 2: Polarization plot for Substrate

A similar curve is seen for Al₂O₃ – 13% TiO₂ coating as that of substrate in figure 2. The rise in current density after applying the potential on the reference electrode is seen. The narrow region in the curve indicates the tendency of corrosion. The values of $E_{corr}$ and $I_{corr}$ are defined from the curves using the Tafel extrapolation technique. Upon reversing the potential scan, the current exhibits, a positive hysteresis loop which symbolizes the phenomenon of pitting corrosion [45].

Figure 3: Polarization plot for Al₂O₃ – 13% TiO₂ coating
The curve obtained in figure 4 is different from the polarization curves in figure 3-4. In figure 4 a gradual increase is seen in the current density with the applied potential. The wide region in the polarization curve do not allow the formation of hysteresis loop. The polarization curve of Cr2O3 coating shows low corrosion current density in comparison to the Al2O3 - 13% TiO2 coating and substrate. The wider region of the curve corresponds to a little formation of pits and a lower absorption of negative chloride ions. The high protection against corrosion is observed in the Cr2O3 coating [46]. The hysteresis loop formation is observed in Figure 2 and Figure 3 for substrate and Al2O3 – 13% TiO2 coating. The formation of hysteresis loop in potentiodynamic polarization curve represents a delay in re-passivation of pit during scanning in negative direction [47]. The lag in repassivation influence the pitting corrosion in substrate and Al2O3 – 13% TiO2 coating. The formation of no such hysteresis loop was observed in Cr2O3 coating. The anodic polarization curves indicate better corrosion resistance than substrate and other coating.

Table 3: Corrosion parameters extracted from anodic polarization curves using Tafel extrapolation method

|       | Icorr (A.cm²⁻²) | Ecorr (V) | βa | βc | Rp (kΩ.cm²⁻²) | C.R. (cm/y) | C.R. (mpy) |
|-------|-----------------|-----------|----|----|---------------|-------------|------------|
| Cr2O3 | 0.00078337      | 0.21894   | 0.00071742 | 0.00075608 | 36.3671689   | 0.00128081 | 0.504256158 |
| Al2O3-13%TiO2 | 0.00081889 | -0.16971 | 0.00072111 | 0.00066939 | 34.5633312   | 0.00133889 | 0.527120422 |
| Substrate | 0.00093238       | -0.047    | 0.000092347 | 0.00048925 | 36.2251909   | 0.00152444 | 0.600174064 |

The corrosion rate for Cr2O3, Al2O3 – 13% TiO2 coating and substrate was 0.504 mpy, 0.527 mpy and 0.600 mpy (mils per year). The best corrosion resistance was shown by Cr2O3 coating due to minimum corrosion rate.

3.3. Micrographic analysis after corrosion
Figure 5 illustrates the SEM micrographs of surface and EDS analysis of substrate after 2 hours’ corrosion in the simulated marine environment.
Figure 5: Surface morphology and EDS analysis after 2 hours of corrosion: (a) SEM micrograph and composition of Substrate, (b) SEM micrograph and composition of Al₂O₃ – 13% TiO₂ coating, and (c) SEM micrograph and composition of Cr₂O₃ coating.

The surface of substrate was highly affected by the corrosion with greater extent of abruption and defects like cracks are seen in figure5 (a). The increase in ferrous content and oxides indicate the corrosion and
rust formation on the substrate surface. The effect of highly corrosive solution on surface of $\text{Al}_2\text{O}_3 - 13\% \text{TiO}_2$ coating is seen in figure 5 (b). The micrograph has much different surface morphology and elemental composition than in figure 1(a). The earlier studies also proved that corrosion mainly occurred on uncoated steel substrates as electrolyte reaches the surface through pores or permeable defects [48]. The EDS analysis depicted greater presence of Fe content in $\text{Al}_2\text{O}_3 - 13\% \text{TiO}_2$ coating in comparison to $\text{Cr}_2\text{O}_3$ coating. Also, a very little change in microstructure of $\text{Cr}_2\text{O}_3$ coating was seen in figure 5 (c) when compared to figure 1 (b). There was least corrosion observed in $\text{Cr}_2\text{O}_3$ coating. The protection of substrate is enhanced using the $\text{Cr}_2\text{O}_3$ coating in marine environment.

4. Conclusion

The following conclusions are drawn from the present study:

1. The coatings on the mild steel substrate protected the surface by the direct attack of electrolyte in 3.5% NaCl environment.
2. The minimum corrosion rate of 0.504 mpy was seen in $\text{Cr}_2\text{O}_3$ coating followed by 0.527 mpy corrosion rate in $\text{Al}_2\text{O}_3 - 13\% \text{TiO}_2$ coating. The comparison of corrosion rates of $\text{Al}_2\text{O}_3 - 13\% \text{TiO}_2$ coating, $\text{Cr}_2\text{O}_3$ coating and mild steel substrate by potentiodynamic polarization method, revealed, best corrosion resistance in $\text{Cr}_2\text{O}_3$ coating.
3. The coatings exhibited low corrosion rates in comparison to the substrate. The average porosities of coatings were 2.293% and 1.69% for $\text{Al}_2\text{O}_3 - 13\% \text{TiO}_2$ and $\text{Cr}_2\text{O}_3$ coating respectively.
4. The order of corrosion resistance for uncoated and coated samples is as follows: $\text{Cr}_2\text{O}_3 > \text{Al}_2\text{O}_3 - 13\% \text{TiO}_2 > \text{Uncoated}$.

Conflicts of Interest: “The authors declare that they have no conflicts of interest to report regarding the present study.”

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