Marine corrosion behavior of EH 36 steel in the Black Sea

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Abstract. The marine environment is a very aggressive environment for metallic materials, especially for unprotected carbon steel. The steel have a low corrosion resistance in harsh corrosive environment like seawater. However, the most equipments and marine structures are made from carbon steel. The Black Sea is brackish water with low salinity. Due to higher-strength and added excellent toughness and formability, The High Strength Low Alloy (HSLA) steel EH36 is used in shipbuilding and other marine structures. This paper present a comparative investigation regarding the corrosion resistance of: i) uncoated EH36 naval steel, ii) coated EH36 naval steel with a two-component polymeric primer and iii) EH 36 naval steel coated with two-component polymeric primer modified by adding of TiO2 nanoparticles. All three surfaces of steel have been investigated in seawater collected from the Black Sea. In situ electrochemical measurements as: open circuit potential (OCP), polarization resistance (Rp), potentiodynamic polarization (PD) and cyclic voltammetry polarization (CV) were performed to monitor the corrosion process. The results show the improved corrosion resistance of polymeric coatings in marine environment compared with uncoated naval steel.

1. Introduction
Nowadays the high strength low alloy (HSLA) is used to increase the lifetime of marine structures like vessels, bridges, onshore and offshore infrastructures [1]. The EH36 HSLA steel is a material for marine structural applications, especially for ship hull manufacturing. These steels contain low carbon, and appropriate amounts of nickel and copper to provide the necessary strength and toughness properties, together with good weldability and corrosion resistance [2].

Marine corrosion is very aggressive environment for the metallic materials, due to the high salt content and low electrical resistivity of seawater. The chloride ions present in seawater depassivate metal and alloys even in absence of oxygen. Chloride ions are also present in marine atmospheres, which can lead to corrosion of non-submerged materials and structures but which work in marine environment [3].

Generally, metals protection against corrosion can be performed by using different methods, such as, anti-corrosion organic, inorganic coatings or cathodic protection [4, 5].

Organic coatings are the most often and commonly used anti corrosion techniques. Organic and inorganic coatings provide passive barrier against the aggressive environment such as marine environment [6].

Coatings containing anti-corrosive agents are applied on metallic surfaces to provide barrier in between the metallic surface and corrosive agents [7].

Among the different inorganic particles used like anti corrosive agents, TiO2 particles are more...
promising because of their unique properties like good corrosion resistance, mechanical properties, thermal stability, nontoxicity and good compatibility with other materials [8].

2. Experimental procedures

2.1. Materials and methods
EH36 HSLA steel plates with 3 mm thickness were painted with two different layers as it is shown in Table 1.

| Samples code     | Description                                                                 |
|------------------|-----------------------------------------------------------------------------|
| EH36             | Uncoated EH 36 HSLA steel                                                  |
| EH36EP           | Primer: Two-component polyamides adduct cured, high solids, high build epoxy primer. |
| EH36EP mixed with TiO₂ nanoparticles | Primer: Two-component polyamides adduct cured, high solids, high build epoxy primer, blended with TiO₂ nanoparticles. |

Chemical composition of the EH36 steel substrate is presented in Table 2. The depth of harvesting of the high water used as electrolyte was 5 meters. A geographic coordinates of the harvest site was: 44050’30.6 latitude and 29045’31 longitude. Parameters of interest for sea water collected from the Black Sea are presented in Table 3.

Corrosion tests were conducted on EH36 naval steel untreated and coated as follows: (i) epoxy primer and (ii) epoxy primer mixed with TiO₂ nanoparticles. In order to maintain the same active sample surface area, they were cut to size 35 x 15 x 3 mm.

| Material | C     | Mn   | Si  | P    | S    | Al   | Nb   | V    | Ti   | Cu   | Cr   | Ni   | Mo   |
|----------|-------|------|-----|------|------|------|------|------|------|------|------|------|------|
| EH36     | 0.06  | 0.38 | 0.25| 0.01 | 0.004| 0.024| 0.04 | 0.05 | 0.02 | 0.02 | 0.02 | 0.02 | 0.01 |

The thickness of polymeric primer (dry thickness - DFT) is equal to 100 μm. Same thickness of coating was used for cover the samples of EH 36 with epoxy primer blended with TiO₂ nanoparticles. Samples used in the corrosion experimental protocol, have been connected with electric cable and covered with high insulation resin to obtain a measurable active area. The active areas of naval steel samples firstly were degreased with alcohol followed by acetone treatment. The samples modified with epoxy primers on surfaces have been degreased with a solution composed with distilled water and special detergent.

| Salinity [PSU] | Electrical conductivity [S/m] | pH |
|----------------|------------------------------|----|
| 15,2983        | 2.22                         | 8.43 |

In the corrosion tests a standard electrochemical cell with three electrodes was used. The test samples are used as a working electrode, the auxiliary electrode is a Pt-Rh network and an Ag/AgCl reference electrode (saturated KCl solution, E = 199 mV vs. normal hydrogen electrode - NHE). The device was a PGZ 100 Potentiostat / Galvanostat and all data were acquired with the VoltaMaster 4 interpretation software.
3. Results and discussions

3.1. Open circuit potential (OCP)

The corrosion tests started by monitoring the evolution of open circuit potential after immersing the samples in sea water until they reached the stationary state. The OCP measurements potential vs. time evolution of the three different surfaces that were studied in sea water are presented in Figure 1. The OCP evolution tendency of uncoated EH36 steel slightly decreased from a value of -638 mV to -686 (mV vs. Ag/AgCl) throughout immersion time. The potential of the OCP was recorded for 250 minutes for each sample. The shift of potential in the negative direction shows that the material is not able to form a protective oxide film on steel surface after it interaction to marine environmental conditions [9-10].

In the case of EH36 coated with epoxy primer (EH36EP), a slight decrease from E= -417 mV to - 519 (mV vs. Ag/AgCl) is observed in the OCP measurement, and the steady state potential for this material is achieved after 190 minute.

The constant potential of epoxy primer coated have an approximately value around E= -518 mV vs. Ag/AgCl, is linked with an enhanced corrosion resistance, being more noble than that of untreated steel. For EH 36 coated with TiO2 nanoparticles mixed with epoxy primer it is observed that the value of OCP tend towards more positive value from E = -288mV to -442 mV.

![Figure 1. Variation of open circuit potential during 250 min. from immersion time for: (1) uncoated EH36, (2) EH36 coated with epoxy primer,(3) EH 36 coated with epoxy primer and mixed with TiO2 nanoparticles.](image)

It is stated in literature that a steady potential is a good indicator that shows intact and protective film stable in time. When comparing the three different surfaces EH 36 steel (in sea water) in terms of steady state potential, it is obviously shown that the untreated EH36 HSLA steel does not reach a steady state potential, but in the case of the two epoxy primer coatings applied on EH36 HSLA steel the anticorrosion performance is improved.

3.2. Linear polarization resistance

The polarization resistance (Rp) evolution is evaluated by measuring linear polarization curves near free potential value. For steady state surface the potential difference is very small (+40 mV). On each
of this curve the Tafel processing is applied, resulting the values of polarization resistance. Linear polarization resistance monitoring is an effective electrochemical method of measuring corrosion which allows determining almost instant the corrosion rate.

The $R_p$ value corresponding to untreated EH36 naval steel remains constant during the immersion time in sea water being equal to mean value of $1.39 \text{ kohm} \cdot \text{cm}^2$.

By applying the polymeric epoxy primer to protect the EH36 HSLA naval steel surface the $R_p$ value increases to a mean value around $366 \text{ kohm} \cdot \text{cm}^2$, being much higher than that of untreated EH36 HSLA naval steel, Figure 2 (a, b).

The $R_p$ value of EH36 HSLA coated steel with TiO$_2$ nanoparticle is higher as compared with coated steel with primer. The mean value is around $670 \text{ kohm} \cdot \text{cm}^2$. The increase of polarization resistance means the decrease of corrosion current, therefore the decrease of corrosion rate. From Figure 2 it can be observed that the primer coated steel as well as coated with nanocomposite primer increases the polarization resistance 100 times. The blended primers show a higher polarization resistance as compared with epoxy primer without TiO$_2$ nanoparticles. These results suggest that the two types of polymeric coatings increase the corrosion resistance of EH36 naval steel and are in good agreement with the evolution of open circuit potential during immersion time.

3.3. Potentiodynamic polarization

The current - potential or $I = f (E)$ curves (potentiodynamic curves) were recorded in the potential domain ranging from -1500 mV to +1500 mV versus Ag /AgCl at a scanning rate of 5 mV/s. Potentiodynamic polarization diagrams were performed for the evaluation of the corrosion performance of EH36 steel, EH36 coated with epoxy primer and EH 36 coated with epoxy primer blended with TiO$_2$ nanoparticles. The recorded diagrams are shown in Figure 3 in logarithmic scale for current density and Figure 4 in linear scale for current density versus potential.

For EH36 uncoated steel, hydrogen reduction activity is observed in the cathodic domain and oxygen reaction blended with anodic dissolution of steel in the anodic domain. The increasing of current density is understood as the destruction of the passive film during the oxidation process. The corrosion current density calculated from polarization diagrams of untreated naval steel is $83.60 \mu \text{A} / \text{cm}^2$, Figure 3, curve (1).

For the EH36 coated steel with primer, the corrosion current density is lower, having a value of $112.57 \text{nA} / \text{cm}^2$, Figure 3, curve (2).
Figure 3. Potentiodynamic polarization curves in sea water drown in logarithmic scale of: (1) untreated EH36 naval steel; (2) EH36EP coated with primer and (3) EH36EP coated with primer mixed with TiO_2 nanoparticles.

EH36 naval steel coated with epoxy primer mixed with TiO_2 nanoparticles, the corrosion current density reveals a much lower value of 28.38 nA/cm^2, Figure 3, curve (3).

Figure 4. Zoom of potentiodynamic polarization curves drown in (i-E coordinates) in the low current densities domain of: (1) untreated EH36 naval steel; (2) EH36EP coated with primer and (3) EH36EP coated with primer mixed with TiO_2 nanoparticles.

In Figure 4 it is observed a higher passive domain of naval steel coated with TiO_2 nanoparticles blended primer.
3.4. Cyclic voltammetry
In Figure 5 and Figure 6, the cyclic voltammograms resulted in seawater of the studied surfaces are presented. The potential domain from -1500 mV vs. to +1500 mV and reversed to -1500 (mV vs. Ag/AgCl) was chosen for the recording of diagrams in order to form a complete cycle, with a scan rate of 5 mV/s. The hysteresis aspect specific to uncoated naval steel EH36 indicates that, in marine environment, this material is inclined to develop pitting corrosion and crevice.

When comparing the two types of coated steels with the uncoated naval steel EH36, it is affirmed that pitting corrosion behavior is not found due to the absence of the specific hysteresis.

Figure 5. Cyclic voltammetry polarization curve in sea water for (1) untreated EH36 naval steel.

Figure 5 shows the sensitivity to pitting corrosion of uncoated naval steel EH36, revealed by the increase of the current in the inset of transpassive region, until the potential is reversed. The current density is higher being expressed in mA/cm².

As shown in the Figure 5, the reported curves of polarization of the untreated EH36 naval steel are observed as narrow passive regions.

The end of this region indicates the Epit (pitting potential) of the passive film, which is destroyed and pitting and crevice corrosion initiate on the untreated steel surface.

This is shown by the passive current density rapide increase without oxygen evolution, as an effect of the passivity failure.

The narrow passive regions of untreated EH36 HSLA naval steel show the pitting attack severity, induced by Cl⁻ anions from sea water. On the other hand, the current density is much smaller for the EH36 HSLA steel coated with polymeric epoxy primer coatings on entire studied range of potential, being expressed in μA/cm², Figure 6, and curve (2).

From Figure 6, curve (3) it can be seen that naval steel coated with primer blended with TiO₂ nanoparticles present much higher resistance to corrosion. Practically the polarization curve did not reveal any increase of the current density over entire domain of polarization even on direct polarization curve as well as on reversed curve. These suggest a better stability of this coating and a much higher resistance to corrosion in sea water as compared with primer without blended TiO₂ nanoparticles.
Figure 6. Cyclic voltammetry polarization curve in sea water of: (2) EH36EP coated with primer and (3) EH36EP coated with primer mixed with TiO$_2$ nanoparticles.

The presence of the extended passive domains of polymeric coatings reveal once again a corrosion resistance higher compared with untreated EH36 naval steel.

4. Conclusion

The experimental investigation work and the obtained results clearly demonstrate the very good effect of blending primer coating with TiO$_2$ nanoparticles to protect the naval steel in sea water environment. Untreated EH36 HSLA steel does not able to reach a steady state open circuit potential, having the more negative value, while the both types of epoxy primer coatings applied on EH36 HSLA steel offers improvement in the anticorrosion performance by revealing more positive open circuit potentials. The polarization resistance value corresponding to untreated EH36 HSLA remains constant throughout the immersion time in electrolyte being the smallest one and equal to mean value of 1.39 kohm·cm$^2$.

By applying the polymeric epoxy primer to protect the EH36 HSLA naval steel surface the polarization resistance increases to 366 kohm·cm$^2$, being much higher than that of untreated EH36 HSLA naval steel.

For EH36 HSLA coated steel with epoxy primer blended with TiO$_2$ nanoparticles the polarization resistance value is much more increasing as compared with coated steel with primer. The mean value is around 670 kohm·cm$^2$. The increased value of polarization resistance means a much lower corrosion current density and therefore a much lower corrosion rate.

The primer coated steel as well as coated with primer blended with TiO$_2$ nanoparticles increases the polarization resistance 100 times, therefore acting to reduce the corrosion rate 100 times. It is noted also that the blended primer show a higher polarization resistance as compared with epoxy primer without TiO$_2$ nanoparticles.

The corrosion current density calculated from polarization diagrams of untreated naval steel is 83.60 $\mu$A/cm$^2$.

For the EH36 coated steel with primer, the corrosion current density is lower, having a value in the nanoscale range of 112.57 nA/cm$^2$.

The EH36 naval steel coated with epoxy primer blended with TiO$_2$ nanoparticles, the corrosion
current density reveals a much more lower value in the nanoscale range of 28.38 $nA/cm^2$.

The better behavior of naval steel coated with primer blended with TiO$_2$ nanoparticles is shown by cyclic voltammetry measurements. Practically the polarization diagram did not reveal any increase of the current density over entire domain of polarization even on direct polarization curve as well as on reversed curve. This suggest a better stability of this coating and a much higher resistance to corrosion in sea water as compared with primer without blended TiO$_2$ nanoparticles.

Polymeric coatings of steel structures for use in hostile marine environment applications are essential for reducing the corrosion rate in seawater.

The electrochemical corrosion tests reveal that the primer blended with TiO$_2$ nanoparticles (polimeric matrix nanocomposite coatings) improve significantly the anticorrosion performance of epoxy primer coatings compared with the epoxy primer without TiO$_2$ nanoparticles.

Polymeric coatings increase the lifetime of the steel structures which work in marine environments and could contribute to safety in their exploitation and lower maintenance costs.

5. References

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