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CORROSION RESISTANCE OF ZINC COATED STEEL IN SEA WATER ENVIRONMENT

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ABSTRACT

The life time of metallic materials used in naval transport industry is influenced by their corrosion resistance. For utilization in shipbuilding and offshore construction, metallic materials need to be covered with protective coatings, especially, or different anti-corrosion protection methods need to be used. During the last decades a series of inorganic and organic coatings was developed. Among inorganic coatings, the most used ones are the galvanizing treatments. This paper presents a comparative investigation regarding the corrosion resistance of uncoated low alloy steel and galvanizing steel. Both samples have been subjected to corrosion in sea water harvested from the Black Sea, Mangalia harbor. The electrochemical assays were: open circuit potential (OCP), linear polarization resistance (Rp), potentiodynamic polarization (PD) and cyclic voltammetry. The results obtained by in situ determination were confirmed by optical microscopy. The results revealed an improved corrosion resistance of galvanized steel in natural sea water in comparison with low alloy steel.

KEYWORDS: low alloy steel, galvanizing steel, corrosion behavior, marine environment

1. Introduction

Currently, the development of naval transport industry has become a focus point around the world, which provides a huge marketing demand for the metal used in ocean engineering. Therefore, there would be a great potential to develop metals with low cost and outstanding corrosion resistance to seawater [1] and marine environments [2]. Most metal structures used in sea water (ships, oil platforms, piers, pipelines, etc.) and in close proximity to the oceans are traditionally made of mild low-carbon and low alloy steels and are subject to corrosion, especially if unprotected [3, 4].

Nowadays, people have started to pay more attention to the effect of protective layers on corrosion resistant property, especially after the successful development of high-tensile corrosion resistant steel containing different layers with good anti-corrosion properties and low price. Mild low-carbon and low alloy steels surfaces are coated with different types of layers such as metallic (zinc, lead, chrome, etc.), ceramic (alumina, etc.) or polymeric layers (layers of bitumen, epoxy-based material, etc.) or modified with different passivation treatments (cerium-based [5], tungsten-based [6], tin-based [1] or chromium-based [7], etc.) for protection against rusting.

Galvanized sheet is a type of sheet which consists of mild steel as the base metal but coated with zinc either by hot dip galvanizing process or metallic coating process [8].

Hot-dip galvanized steel is increasingly used in industry as an alternative to non-galvanized cold rolled steel due to its enhanced corrosion resistance. During the last decade, numerous works focused on new galvanized coatings including magnesium and aluminum or a combination of both in the zinc coating [9].

Zinc is widely used for corrosion protection of steel due to its sacrificial aim: its redox potential being more negative (less noble) than that of steel under the same conditions, zinc deposits behave as sacrificial anodes and thus offer a cathodic protection to the steel substrate [5, 10, 11].

The ability of zinc to galvanically protect mild steel and low carbon steel has made this metal important from an industrial point of view. Therefore, the compactness of galvanized coatings, which provide mild steel with good corrosion protection, is essential for the economic utilization of steel. The composition and structure of the protective layer depend on the kinds of alloying metals and corrosion environments containing various anions such as Cl^-, SO_4^{-2}, CO_3^{-2}, and NO_3^-. The good corrosion resistance of hot dip galvanized steel products in natural environments is due to the formation of a protective basic zinc carbonate film on the surface of the zinc coatings [12, 13].

Studies on the corrosion of galvanized steel revealed that its corrosion behavior consisted of three different stages. In stage 1, the electrochemical behavior of galvanized steel is mainly related to the dissolution of the zinc oxide layer which was formed in the air. In stage 2, the surface of the zinc layer is covered with thick, white rust and the underlying steel begins to corrode. During this stage, the corrosion rate of the zinc coating rapidly decreases, accompanied by a shift in the corrosion potential to a more noble potential. In stage 3, the amount of red rust on the coating surface rapidly increases; the galvanized steel shows almost the same corrosion potential as that of carbon steel, even though the zinc coating is still covering a few parts of the steel reinforcement. The underlying steel corrosion progresses by dissolution of iron and, therefore, at this stage, the zinc coating no longer acts as a sacrificial anode [14].

The aim of this paper was to investigate the corrosion behavior of the low alloy steel and galvanized steel in seawater by electrochemical methods. The attempts are to evaluate the contribution of zinc layer deposited on low alloy steel to the corrosion resistance in seawater environment.

2. Experimental set-up

The corrosion experiments were performed on low alloy steel and galvanized steel, which were purchased from Arcelor Mittal Galati, Romania. The mean zinc coating thickness was 6.5 µm.

All samples were cut to dimensions of 25x25x2 mm. Before any experiments, the samples have been bonded with cooper wire and isolated with epoxy resin to obtain a measurable active surface area. The samples were degreased with acetone and alcohol and rinsed afterwards with deionized water.

The experiments were done using a Potentiostat–Galvanostat PGZ 100 and the data were recorded with VoltaMaster software. In order to perform the corrosion experiments it was used a standard three-electrode cell consisting of the tested samples as working electrode, a Pt-Rh grid used as auxiliary electrode and Ag/AgCl electrode (saturated KCl solution, E = -200 mV vs. normal hydrogen electrode (NHE)) as a reference electrode.

As corrosive environment it was used sea water harvested from the Black Sea, Mangalia port area and its characteristics are shown in Table 1.

***Table 1**. Black Sea water characteristics*

pH	**Salinity** [ppt]	**Conductivity** [mS]
7.63	12.4	21

The in-situ applied electrochemical methods were: open circuit potential (OCP), linear polarization, polarization resistance, potentiodynamic polarization and cyclic voltammetry.

The surfaces were investigated on an optical microscope type OPTIKA XDS-3MET before and after corrosion tests in order to estimate the corrosive effects. The optical image was performed with software Vision Pro Plus Ver 5.0 on computer connected to an optical microscope.

3. Results and discussions

3.1. Open circuit potential

The evolution of the steady state interface between uncoated steel or galvanized steel and the corrosive environment was evaluated by measuring the open circuit potential of both surfaces during immersion time in sea water. In Fig. 1 there are presented both diagrams obtained during one hour when it was reached a steady state value of free potential explained by an equilibrium of metallic interface and corrosive sea water solution.

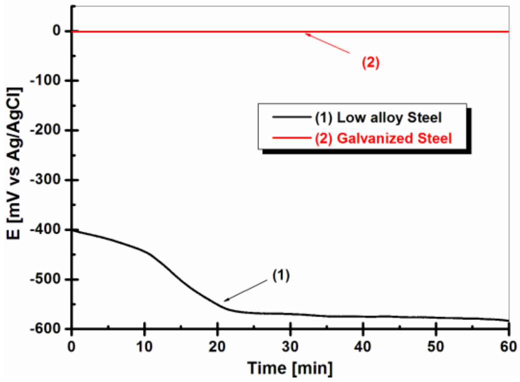

***Fig.1**. Variation of open circuit potential during immersion time in sea water: (1) - Uncoated steel and (2) - Galvanized steel*

From Fig. 1. it can be seen that for low alloy steel the potential drops down in the first 30 minutes from -400 mV vs. Ag/AgCl to -575 mV vs. Ag/AgCl and after that it reaches a stable value. This behavior indicates a high instability and changes on its surface because of the corrosion process and corrosion products. This type of potential behavior was observed by S.S. Xin et al [15] when studied the corrosion behavior in hot concentrated sea water of 316 stainless steel.

For galvanized steel the potential remains constant with the value around 0 mV vs. Ag/AgCl, for the same immersion period. This aspect is correlated with an improved corrosion resistance by the zinc layer on the steel surface.

Generally, the steady state potential indicates that the zinc layer remains intact and protective. Comparing the steady state potentials presented in Fig. 1 it can be clearly observed that the galvanized steel offers improved corrosion resistance in comparison with untreated low alloy steel.

3.2. Measuring the polarization resistance (Rp) values during immersion time

The evolution of polarization resistance during immersion time was evaluated by measuring the linear polarization curves around the open circuit potential value with a very small potential amplitude (± 40 mV) to preserve the steady state balance obtained at the interface between metallic samples and corrosive environment. The polarization resistance values of low alloy steel and galvanized steel immersed in sea water are presented in Fig. 2 (a).

From Fig. 2 (a). it can be observed that the low alloy steel has the lowest polarization resistance (Rp) being equal to *1.35 kohm.cm*^{2}. By applying a zinc layer on the low alloy steel surface, the polarization resistance increases to a mean value of *2.1 kohm.cm*^{2}. By increasing the value of polarization resistance, the corrosion current density decreases and therefore the corrosion rate is lowered, as it can be seen in Fig. 2 (b).

Fig. 2 (b). illustrates the evolution of corrosion rate in time, corresponding to the polarization resistance (Fig. 2 (a)) for both analyzed surfaces immersed in seawater.

According to the data presented in Fig. 2 (b) it can be observed that for the low alloy steel, which has the lower polarization resistance, it corresponds the higher corrosion rate in comparison with the corrosion rate of galvanized steel.

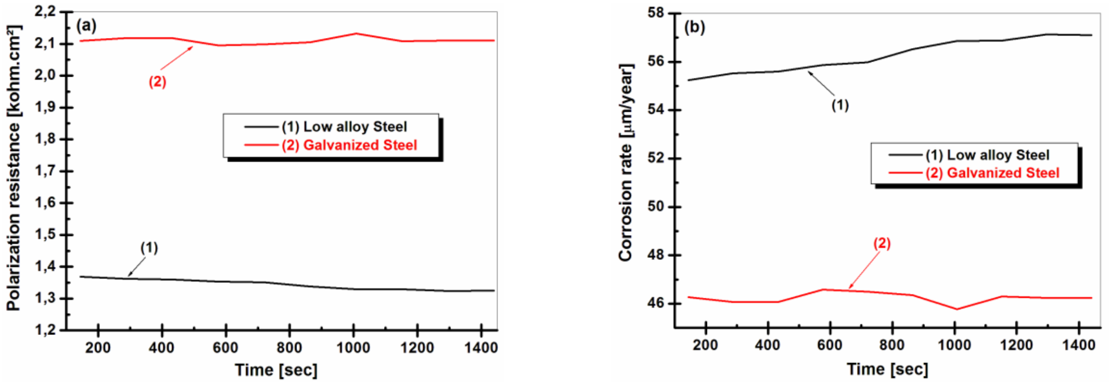

Fig. 2. *The evolution of polarization resistance (Rp) values during the immersion time for: (1) uncoated steel and (2) galvanized steel*

These results suggest that the zinc layer increases the corrosion resistance of low alloy steel and are in good agreement with the evolution of open circuit potential values.

3.3. Potentiodynamic polarization

The effects of natural sea water environment on the corrosion rate of galvanized and low alloy steel samples were studied using Tafel polarization technique. Fig. 3. presents typical E-log *i* polarization curves which were recorded in a range of potentials starting from -1.5 V vs. Ag/AgCl to -0.5 V vs. Ag/AgCl at a potential sweep scan of 5 mV/s for both samples immersed in natural sea water. The corresponding corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic slope (b_a) and cathodic slope (b_c) are presented in Fig. 3.

From the data plotted in Fig. 3 it can be observed for both metallic surfaces the anodic dissolution of iron or zinc and the cathodic hydrogen evolution reaction in natural sea water.

The calculation of the Tafel slopes and the current densities (as corrosion rates) from polarization potentiodynamic curves are also presented in Fig. 3

for low alloy steel and galvanized steel. Fig. 3 indicates that the zinc coating shifts the corrosion potential (E_{corr}) to the more negative direction without affecting anodic dissolution, which leads to a significant decrease of corrosion current density (corrosion rate).

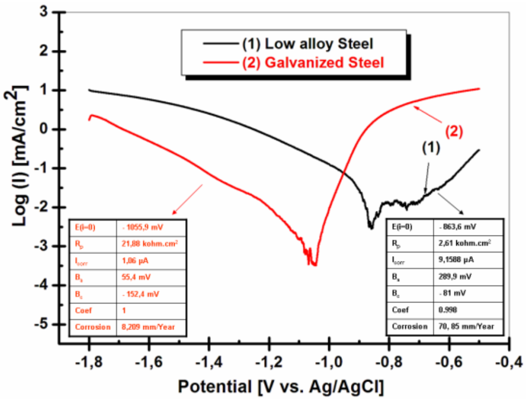

***Fig. 3**. Tafel representation of potentiodynamic polarization for uncoated and galvanized steel immersed in natural sea water*

From Fig. 3 it can be also seen that the corrosion current (i_{corr}) of uncoated steel is higher than the corrosion current of galvanized steel which results in a decrease of the corrosion rate from 279.5 µm/year for uncoated steel to 8.24 µm/year for zinc layer over carbon steel, in natural sea water.

3.4. Cyclic voltammetry

The cyclic voltammograms for low alloy steel and galvanized steel were recorded in the potential range from -1.5 V vs. Ag/AgCl to -0.5 V vs. Ag/AgCl at a scan rate of 5 mV/s and then reversed with the same scan rate till the starting potential. The cyclic voltammograms for both studied surfaces are presented in Fig. 4. From Fig. 4 it can be seen that upon the onset of the transpassive region, the current still raises up until the potential is reversed in the case of galvanized steel in natural sea water solution. On the other hand, the current of the transpassive region decreases for low alloy steel, forming a reduced anodic peak and this behavior can be attributed to the rust layer formed on the surface.

The highlighting of the localized corrosion susceptibility in the presence of chloride ions in the sea water of galvanized steel can be seen very well due to the specific hysteresis aspect which is present in the anodic transpassivation part of the plotted curve (1) in Fig. 4.

At the end of the narrow passive region for galvanized steel, the pitting potential breaks down the passive film and pits initiate on the zinc layer surface. This is indicated by the rapid increase in the passive current density without any sign for oxygen evolution, as a consequence of the passivity breakdown. The low alloy steel has revealed the expanded passive domain due to the formation of a rust layer and the appearance of general corrosion. This type of comportment was observed by K. M. Zhody *et al.* [16] when they studied the corrosion behavior of leaded-bronze in sea water.

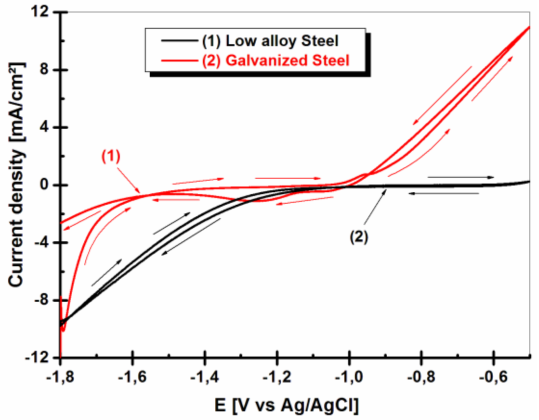

***Fig. 4**. Cyclic voltammograms in sea water for: (1) uncoated steel and (2) galvanized steel*

3.5. Optical microscopy

Ex-situ investigations of surfaces were performed with an optical microscope. In Fig. 5 are presented the optical micrograph of low alloy steel and galvanized steel before and after electrochemical assays.

From Fig. 5 (a) it can be observed that the low alloy steel before the corrosion study has a non-uniform surface, the marks of atmospheric corrosion attack being visible, in special pitting corrosion.

For galvanized steel, in Fig. 5 (b) before electrochemical tests there are shown the marks of zinc flow produced in hot dip galvanizing treatment. The low alloy steel after electrochemical tests presents a surface with generalized corrosion (Fig. 5 (c)) and significant amounts of corrosion products (rust). For galvanized steel (Fig. 5 (d)), it can be observed only the pitting corrosion with small diameter pits which confirm the results of cyclic voltammetry tests.

The overall electrochemical corrosion results confirm the improving of corrosion resistance offered by the galvanizing treatment to form a zinc layer on the low alloy steel surface.

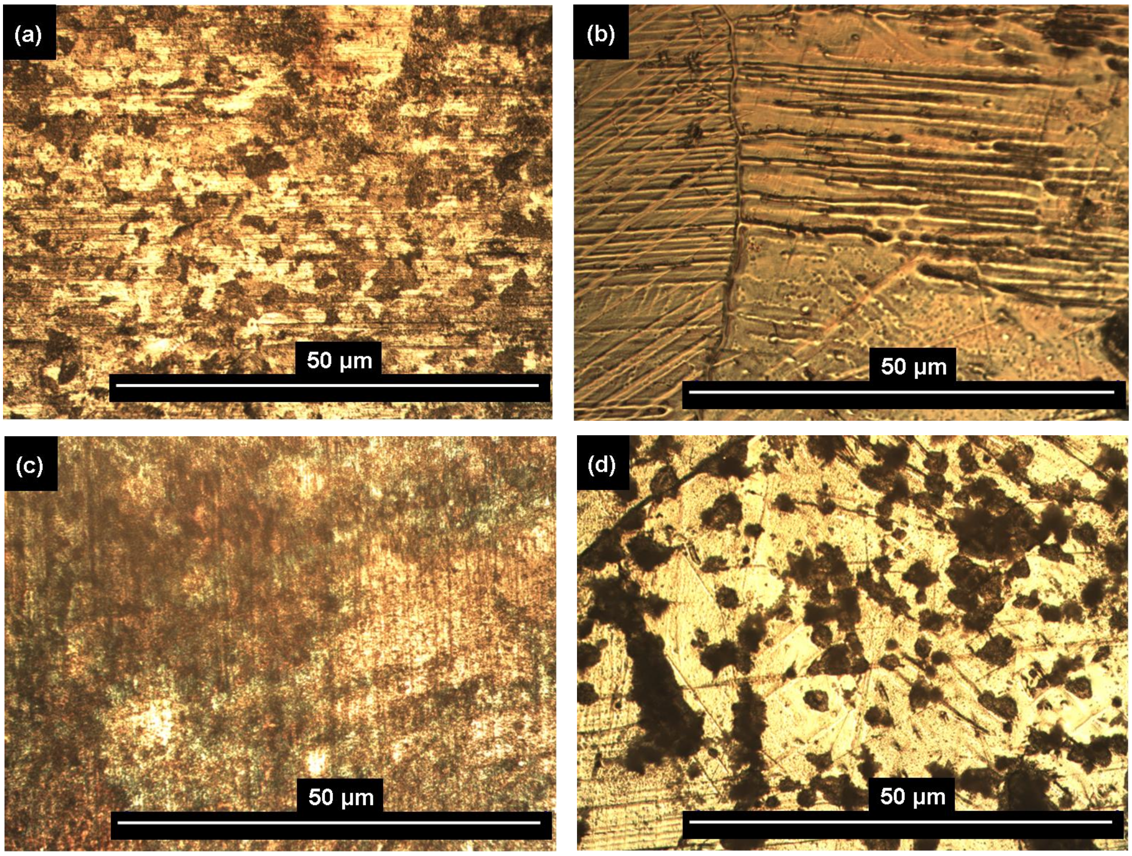

Fig. 5*. Optical microscopy of low alloy steel: (a) before corrosion and (c) after corrosion and galvanized steel: (b) before corrosion and (d) after corrosion*

4. Conclusion

In this paper it was studied the corrosion behavior of low alloy steel and galvanized steel in natural sea water. From the results offered by the electrochemical methods used in our research, the following conclusions can be drawn:

- the zinc coating improves the polarization resistance of steel comparatively to uncoated low alloy steel suggesting an increase of corrosion resistance. The higher corrosion rate corresponds to low alloy steel as compared to galvanized steel.

- from the Tafel representation of potentiodynamic polarization diagrams, it can be observed that the decrease of current density is associated to the decrease of corrosion rate for galvanized steel.

- the cyclic voltammograms reveal a higher susceptibility to pitting corrosion for galvanized steel as compared to low alloy steel which presents higher general corrosion.

- the zinc coating increases the lifetime for naval steel and this is materialized in lowering maintenance costs.

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