Studies on galvanic corrosion of metallic materials in marine medium

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Abstract. Galvanic corrosion occupies an important place among the corrosion techniques studies, especially because harbors and naval installations presents multiple components which are in direct contact with saltwater during operation time, such as: boats propeller - bronze, ship hull - carbon steel, rivets - steel, different types of protection shields - aluminum etc., thus metallic types combinations increase selective erosion depending on the metal position in the galvanic series. The galvanic corrosion prevention can be achieved by local cathodic protection with pieces of electronegative metal (zinc, magnesium) placed near the contacts or by inserting between these two metals of one or multiple high corrosion resistance materials to that specific medium. This paper presents an experimental study on different metal couplings in Black Sea water corrosion medium, in order to highlight the anodic (oxidation) or cathodic (reduction) protection of each metal during coupling.

1. Introduction

Marine corrosion represents a permanent problem, not only for moving or stationary ships, but also for all the industrial equipment’s and constructions used in a harbor that come in contact for a long period of time with salt water and the marine medium. Approximately 90% of corrosion losses are related to ferrous materials used at road bridges construction, structural reinforcements, railways and different types of ships.

During marine mediums effects on metallic structures analyses, at least five corrosion zones can be highlighted: the area exposed to marine atmosphere, the spraying area, the waves (water / air) area, the totally underwater area and the area exposed to the water saturated soil. The highest corrosion rate take place on the spraying and the waves areas, because the steel is exposed directly to the oxygen from the air [1-4]. On the steel pillars and ship’s hull totally underwater area, a protective layer of marine deposits covers the surface. In addition, because of the high concentration of $HCO_3^-$ ions from the salt water, calcareous deposited are formed on the metal surface, which acts as obstacles against the oxygen diffusion.

The sea water corrosivity depends on multiple factors [5], such as: salinity, dissolved oxygen, temperature, different types of biological factors [6] (bacteria, fungus, algae), relative displacement of corrosion medium, exposed type of metal. The type of corrosion that may occur depends, especially, on the metallic material subjected to the action of seawater and, secondly, on all the presented factors. The marine medium corrosion is known as being electrochemical, because it is based on electron transfer reactions, in fact, the entire process reflects the simultaneous development of two processes;
the anodic process (oxidation) and the cathodic process (reduction). Therefore, this is a wet corrosion that can present different types of effects. By the bimetallic corrosion, all the metals can be classified in a certain order, known as galvanic series, which take into consideration the electric potential developed.

In a bimetallic couple, the less noble material will become the anode, therefore, the degradation rate will be higher compared to that of the decoupled state. Also, the noble material will act as a cathode in that corrosion cell.

Galvanic corrosion is considered as one of the most common forms of corrosion, as well as one of the most destructive form [7-12].

2. Experimental materials
This research is focused on analyzing the corrosion behavior in galvanic couplings of ferrous alloys and non-ferrous alloys, used in ships manufacturing and harbor constructions which get in contact with the marine medium [13-18].

The chemical compositions of all samples were analyzed by means of a Foundry-Master Spectrophotometer - World Wide Analytical Systems AG. The elemental chemical compositions of low-alloy steels (1, 2, 3, 4, 5), hot rolled stainless steel (SS), phosphorous cast iron (PCI), Cu-Sn bronze, Cu-Zn-Al shape memory alloy (AFM) and aluminium alloy (DURAL) used samples are presented in Table 1.

| Table 1. Chemical composition of analyzed samples. |
|-----------------------------------------------|
| Alloy             | Chemical element, wt %       | CE |
|                  | C    | Si   | Mn   | P    | S    | Al   | As   | Ti   | Cu   | Ni   | Cr   | Mo   |
| STEEL 1          | 0.17 | 0.22 | 0.75 | 0.02 | 0.01 | 0.005| -    | -    | 0.02 | 0.02 | 0.05 | -    | 0.30 |
| STEEL 2          | 0.16 | 0.21 | 1.34 | 0.01 | 0.008| 0.02 | 0.01 | 0.01 | 0.03 | 0.02 | 0.01 | 0.002| 0.40 |
| STEEL 3          | 0.12 | 0.32 | 1.10 | 0.02 | 0.01 | 0.04 | 0.007| 0.004| 0.03 | 0.22 | 0.04 | 0.004| 0.03 |
| STEEL 4          | 0.17 | 0.31 | 1.38 | 0.02 | 0.02 | 0.06 | -    | 0.006| 0.02 | 0.11 | 0.02 | 0.003| 0.40 |
| STEEL 5          | 0.17 | 0.36 | 1.47 | 0.02 | 0.01 | 0.08 | 0.01 | 0.007| 0.03 | 0.01 | 0.01 | 0.004| 0.43 |
|                  | Alloy | Fe   | C    | Si   | Mn   | P    | S    | Cr   | Ni   | Ti   | Fe   |
| SS               | 71.58| 0.046| 0.45 | 1.16 | 0.028| 0.006| 17.12| 9.03 | 0.569| 71.58|
| PCI              | 91.76| 4.50 | 1.54 | 1.03 | 0.620| 0.140| 0.097| 0.057| 0.148| 0.012| 0.016| 0.050| 0.029|
|                  | Alloy | Cu   | Sn   | Pb   | Zn   | Fe   | Al   | Ni   | Si   | Mn   |
| BRONZE           | 85.62| 11.20| 1.05 | 1.39 | 0.40 | 0.02 | 0.29 | 0.02 | 0.01 |
| AFM              | 69.76| 23.7 | 6.26 | 0.005| 0.014| 0.003| 0.017| 0.420| 0.075| 0.005| 0.010| 0.003| 0.015|
| DURAL            | 90.3 | 5.41 | 2.26 | 1.50 | 0.169| 0.223| 0.039| 0.029| 0.015| 0.013| 0.007| 0.003| 0.002|

The alloys microstructural analyzed has been realized according to the standard procedure [7], after mechanical polishing and surface attack with 2% nitric acid in ethyl alcohol solution by means of an OLYMPUS PME3 metallographic microscope.

The samples metallographic images of the attacked surface are shown in Figure 1. As can be seen from the images, all the studied samples present; a hypoeutectoid structure where the light areas represent the polygonal, equiaxed grains of ferrite (Fα) and the dark areas represents perlite (a mechanical mixture of 88% ferrite and 12% cementite), (Figure 1a, b, c, d, e).
Figure 1. Low-alloy steel samples microstructure, 3000X: a) STEEL 1 sample; b) STEEL 2 sample; c) STEEL 3 sample; d) STEEL 4 sample; e) STEEL 5 sample; f) Phosphorous cast iron sample, 400X; g) Bronze, 500X; h) Shape memory alloy, 500X.

In the phosphorous cast iron metallographic image, eutectic phosphorus (ternary eutectic formed by ferrite, cementite and iron phosphide), can be seen alongside graphite, ferrite and perlite (Figure 1f). The bronze sample has Sn as the main alloying element. This sample presents a biphasic structure, α + β, which is specific to cast alloys (Figure 1 g). The Cu-Zn-Al shape memory alloy presents uneven equiaxial grains, because the structure is, basically, given by the heat treatment (Figure 1h).

The experiments were performed in accordance with the occupational health and safety laws and regulations in order to eliminate all the risks and dangers which can affect the human resource during the experiment procedures [19-22].

3. Corrosive medium selection
Sea water represents approximatively 70% of the earth's surface, being one of the most abundant but, also, one of the most corrosive natural electrolytes [23-25]. This substance attacks most of ships and harbor constructions metals parts, its effects on the metal structures can be different depending on the exposed area of the metal, if it is completely underwater, in the spraying area, the waves area or exposed completely to the marine atmosphere [26-28].

In the waves area carbon steels and low alloy steels are highly affected by corrosion while stainless steels withstand longer to marine corrosion. Also, austenitic stainless steels present better behavior than martensitic or ferritic ones.

In the underwater area, in addition to the seawater effects, corrosion is influenced by the dissolved oxygen presence and concentration, temperature (oxygen concentration decreases with the increase of temperature, while the rate of electrochemical corrosion increases), plants and microorganisms, saline deposits, pollutants in coastal areas etc. Sulfate reducing bacteria can increase the sulfur dioxide concentration, which is extremely aggressive especially for steels and copper-based alloys. However, the corrosion in the waves area is much higher than that from the underwater area [29].

The exposing time plays an important role in the corrosion rate, but this, also, depends on the reaction products properties (adhesion, porosity, solvent permeability, solubility etc.).

In this paper, the corrosion degradation and effects on ferrous and non-ferrous alloys exposed to Black Sea water, at normally boundary condition has been studied.

The salt water used in this study has been collected from Black Sea, in the Romania-Constanța-Agigea seaside area during June and July. The solution characteristics and chemical composition


$\left( g \cdot L^{-1} \right)$ are as follows: Cl$^-$ – 8.26; HCO$_3^-$ – 0.183; CO$_3^{2-}$ – 0.022; SO$_4^{2-}$ – 1.137; Na$^+$ – 4.47; K$^+$ – 0.158; Ca$^{2+}$ – 0.203; Mg$^{2+}$ – 0.557 salinity 15.0 $g \cdot L^{-1}$ and pH = 7.1.

4. Equipment and methods

The simplest method of analyzing the corrosion rate of a metal, involves exposing it to the testing medium and measuring the sample weight losses depending on the exposure time.

Basically, the chemical processes that occurs during corrosion are based on electron exchange reaction, as follows: electron acceptance is a reduction process and always takes place at the cathode; electrons release is an oxidation process and always takes place at the anode.

By drawing the Tafel plots the following parameters which characterize the corrosion resistance of the investigated samples were analyzed:

- the corrosion potential (E$_0$ [mV]). This represents the chemical equilibrium potential from which the corrosion process starts (as closer as the value of E$_0$ is to 0, the materials are chemically stable and corrosion resistant);
- the cathode curve slope ($\beta_c$ [mV]) and the anode curve slope ($\beta_a$ [mV]). The oxidation / reduction characteristics are highlighted in the Tafel plots on these two branches: the anodic branch, which gives information about the corrosive medium oxidative character and the cathode branch, which provides information about the reduction character;
- the corrosion current density (J$_{cor}$ [$\mu A/cm^2$]). The electrons flow through the corrosion cell influence the corrosion process intensity and is known as the corrosion current. In order to reflect the real corrosion intensity, it should be related to the corroded material surface, this is known as the corrosion current density;
- the polarization resistance (R$_p$ [Ohm·cm$^2$]) can be used for the quantitative description compared to the metal corrosion resistance in different corrosive mediums. If the value of R$_p$ is high than the sample corrosion resistance is high, if this value is low than the studied material will be highly depredated.
- the corrosion rate (V$_{cor}$ [$\mu m/year$]). The corrosion rate is related to the oxidation/reduction reactions which occurs at the anodic and cathodic kinetic level.

In case of galvanic coupling, two metals M1 - M2 submerged in a corrosive liquid, it is observed that the cathodic (reduction) branch, $b_{c_2}$, specific the noble material M2, intersects the anode (oxidizing) branch of the less noble metal M2, meaning that at the presented intersection parameters (E$_{couple}$, J$_{c0}$) M1 metal corrosion and M2 metal reduction occurs (Figure 2).

![Figure 2. Galvanic couple graphic representation.](image-url)

The corrosion potential determination and the cyclic/linear polarization curves testing have been carried out by means of a VoltaLab 21 electrochemical system from the Technical University...
"Gheorghe Asachi", Faculty of Chemical Engineering and Environment Protection "Cristofor Simonescu" from Iasi. The potentiostat used possess special features for polarization resistance determination, long-term corrosion potential determination and pitting corrosion tests. The PGP201 potentiostat (VoltaLab 21) is a potentiostat/galvanostat which includes a built-in signal generator, jointly with an electrochemical acquisition and processing software VoltaMaster, create the so-called VoltaLab Economic Electrochemical Laboratory 21 (Radelkis Copenhagen) (Figure 3).

![Electrochemical cell](image1)

![Reference electrode](image2)

a) Figure 3. a) The Electrochemical VoltaLab 21 system; b) Three electrodes electrolytic cell.

The three electrodes electrolytic cell (Figure 3 b) used in this study consist in a glass 50 to 150 ml volume vessel, a saturated calomel electrode, which presents a Luggin capillary tip, as reference electrode and a platinum wire auxiliary electrode (measuring electrode).

5. Results and discussion
The galvanic corrosion is represented by the corrosive deterioration of two different materials which are coupled in a corrosive electrolyte. It occurs when two (or more) different metals are brought into electrical contact underwater. When a galvanic couple is formed, one of the coupled metals becomes the anode and presents a faster degradation, compared to that presented when it is exposed just by itself, while the other metal becomes a cathode with higher corrosion resistance compared to that presented when exposed just by itself. The driving force for corrosion is a potential difference between the different materials.

In a bimetallic couple, the less noble material will become the anode of the corrosion cell and tend to corrode at higher rate, compared to the decoupled state. The noblest material will act as cathode in the corrosion cell. Galvanic corrosion can be considered as one of the most common forms of corrosion, as well as one of the most destructive form.

The noble character of a material can be analyzed by measuring its corrosion potential. The well-known galvanic series lists the relative noble character of certain materials in seawater. A small anode to cathode ratio is extremely undesirable. In this case, the galvanic current is concentrated on a small anode area, therefore anode is rapidly depredated. Galvanic corrosion problems should be solved by considered from the designing phase of an equipment, in order to avoid these problems. Galvanic corrosion elements can be calculated at macroscopic or microscopic level. Also, to the galvanic currents can be subjected different phases or microstructural features.

Table 2 presents the corrosion potentials (E_corr) and the corrosion current densities (J_corr) for single exposed alloys in Black Sea water, analyzed by linear polarization curves. The corrosion potentials and current densities for the studied galvanic couples between bronze and other alloys in Black Sea water have been analyzed from the overlapping of the current potential-density of single alloys, in logarithmic coordinates J-E (Figures 4 - 6).
Table 2. Corrosion parameters in Black Sea water for single sample.

| ALLOY | BRONZE | STEEL 1 | STEEL 2 | STEEL 3 | STEEL 4 | STEEL 5 | DURAL | AMF | SS | PCI |
|-------|--------|---------|---------|---------|---------|---------|-------|-----|----|-----|
| Ecorr mV | -222   | -617    | -510    | -474    | -569    | -562    | -1134 | -344| -361| -780 |
| Jcorr µA/cm² | 8.11   | 14.6    | 23.1    | 13.6    | 61.3    | 39.0    | 12.7  | 2.99| 8.91| 8.4 |

Figure 4. Galvanic couplings in Black Sea water: a) Bronze – Steel 1; b) Bronze – Steel 2; c) Bronze – Steel 3.

Figure 5. Galvanic couplings in Black Sea water: a) Bronze – Steel 4; b) Bronze – Steel 5; c) Bronze – Phosphorous cast iron.

Figure 6. Galvanic couplings in Black Sea water: a) Bronze – Duralumin; b) Bronze – Shape memory alloy; c) Bronze – Stainless steel.
The corrosion potential as well as the corrosion current density of the galvanic couplings has been analyzed according to the above plots, the results obtained are shown in Table 3.

Figure 6 (c) presents the galvanic couple in sea water of bronze ($E_{\text{cor}} = -222 \text{ mV}$; $J_{\text{cor}} = 8.11 \mu\text{A / cm}^2$) and stainless steel ($E_{\text{cor}} = -321 \text{ mV}$; $J_{\text{cor}} = 0.87 \mu\text{A / cm}^2$). As can be seen, between these two samples there is no galvanic couple, i.e. the alloys do not influence each other when coupled in sea water.

### Table 3. Corrosion potential and the corrosion current density in Black Sea water for coupled samples.

| COUPLE       | BRONZE/STEEL 1 | BRONZE/STEEL 2 | BRONZE/STEEL 3 | BRONZE/STEEL 4 | BRONZE/STEEL 5 | BRONZE/PCI | BRONZE/DURAL | BRONZE/AFM |
|--------------|----------------|----------------|----------------|----------------|----------------|------------|--------------|------------|
| $E_{\text{couple}}$, mV | -619           | -459           | -522           | -552           | -500           | -647       | -599         | -240       |
| $J_{\text{couple}}$, $\mu\text{A/cm}^2$ | 638            | 528            | 540            | 586            | 538            | 746        | 654          | 293        |

According to this study, the bronze is the noble alloy and acts as a cathode, while the steels, the phosphorous cast iron, the aluminum and the shape memory alloy become the anode (the active electrode) in the studied galvanic couples. Thus, when exposed to sea water, which is an aggressive corrosion medium and in the presence of atmospheric air, the transfer of electrons from the less noble alloy to the noble alloy is highly increased; the corrosion rate of the less noble alloy increases while the noble alloy corrosion rate decreases compared to that presented when these are single exposed in sea water. This can be explained by the fact that, for the single exposed alloys, submerged in the electrolyte the current density, the current density is measured at the corrosion potential, i.e. when the sum of the cathodic and anodic reactions on the alloy surface is practically zero (0) and the current flowing through the potentiostat circuit is very low. However, when metals or different alloys are coupled in solution, between the two metals a potential difference appears that stimulates the electrons flowing from the anode to the cathode.

In case of all the galvanic couples analyzed, the couple potential is situated between the corrosion potentials of the coupled alloys, while the corrosion current densities are much higher than those of the less noble alloys. Also, the shape memory alloy shows the lowest influence when coupled with bronze compared to the other studied alloys.

### 6. Conclusions

According to this study:

1. The galvanic corrosion is highly important in areas where different metals parts work in a liquid medium, such as: oil platforms, ships, pumps and petroleum products, ore products, domestic wastewater or industrial wastewater transport pipelines etc.

2. The main objective of this study is to highlight the fact that when two different metals are used in the same assembly, only one remains intact, while the other one present serious degradation.

3. When a bimetallic couple must be protected, a so-called sacrifice anode of nickel, aluminum or zinc can be used.

4. According to the experimental data obtained, the bronze is the noble metal in all the studied couples (steel-bronze, aluminum-bronze, phosphorous cast iron-bronze).

5. In case of the stainless steel-bronze couple, both metals present noble behavior, the intersection of the Evans curve didn’t occur on the oxidation-reduction branches, i.e. the galvanic couple isn’t created.

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