Corrosion Behaviour of Tin Bronze for Shipbuilding Industry

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Bronzes are part of the moving elements of the shipbuilding industry, such as ship propellers, fixtures, flanges, pumps and turbine blades, working both in salt water and in freshwater. In this context, the study regarding shipbuilding elements corrosion in seawater has great importance. The paper includes a chemical and structural analysis of the bronze parts subject to corrosion, using a PGP 201 VoltaLab facility. The cyclic polarization curve was determined. Microstructural analysis was carried out on a tin bronze using scanning electron microscope (SEM) equipped with EDX. Samples were immersed for 40 days in seawater. After that, it was analyzed with optic microscope and by EDX spectroscopy.

Keywords: corrosion, oxides, cyclic voltammetry, electron microscopy

The tin bronze is used in shipbuilding and oil platforms due to the high resistance at both hydro abrasive wear and corrosion in water with high salinity or highly aggressive environments. Oxides resulting from the corrosive action of the working environment create a uniform coating surface and give indications about the type of chemical reactions that took place during use [1-6]. The chemical composition of the superficial layers on the bronze surface was appreciated [1-3] as a mix of compounds from copper or a mix of copper-tin compounds, depending by the environment and the presence of the oxygen, or several chemical compounds from the environment (chlorides, bicarbonates, sulphates and so on), and the exposure time [4-8].

A number of previous studies [9-16] have shown that the formation of the corrosion products is complex, including electrochemical reaction in a multiphase system. Simplifying the previous results it can be admitted that the surface alteration leads to two types of morphology, depending by the aggressiveness of the environment: (1) smooth surface with noble patina, and (2) rough patina, where original surface has been damaged [1-3, 17-22]. For both types was observed inner layer rich in tin, often linked with residual metallurgical structure of the alloy, which is characterized by the presence of oxides of tin and copper [17-22].

Bronze patina has a complex chemical structure resulted from copper reactions on the first place but also on the other elements with the corrosion medium agents. During oxidation of the copper and his alloys on the metal surface oxides are forming, the chemical composition and their structure depends by the electrolyte composition and the immersion time [23]. In neutral solutions the corrosion copper process is controlled by the Cu⁺ diffusion through the oxide layer. For the bronze corrosion, in the same solution type, the simultaneously presence of the SnO₂ and Cu₂O was highlighted, their ratio depending by the immersion type [24].

In marine environments, on the alloy surface, some copper chlorides can be found and the green patina forming can last for 7-9 year, [9, 19, 23]. The tests made on a 20 year period in different marine places, for some copper alloys, have proved a very good corrosion resistance in the marine environment, and the corrosion rate because is very slow – in the range $(1-25) \times 10^4$ mm/year.

The formed copper or bronze patina protects the metal surface against advanced corrosion ensuring its preservation [1-3]. In contrast to steel, copper-based alloys are less susceptible to pitting and to crevice corrosion caused by chloride ions also to temperature dependence for these types of corrosion.

Under normal atmospheric temperature and pressure the bronze forms on the surface a protective layer of passive chemical combinations of oxides and sulphides. This layer is attacked while the piece is merged in sea water (especially the Black Sea water with high salinity). In chemically aggressive media the pitting type corrosion can occur, being destructive (film passivity is destroyed locally). In marine conditions, can occur as a result of corrosion, atacamite type compounds ($Cu_2(OH)_3Cl$) or copper sulphate which can partially fill the pores but unevenly, resulting mass transfer by corrosion [25-28]. In figure 1 is shown a corrosion model [20].



Fig. 1. Qualitative model for the film formed on bronze after exposure to seawaters [29]

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Elements	Cu	Sn	Pb	Zn
[%]	86.36	11.20	1.05	1.39

Bernent Net norm Engr Copper 194027 01.85 08.19 225 Tin 33434 1.2 651 061 Marganese 541 1.2 651 061 Administ 2005 6.2 1.43 001 Marganese 544 014 007 005 Marganese 544 014 003 044 Photphone 1.0 0.02 0.02 0.02 Silcon 40 0.02 0.05 0.03 0.03

Fig. 2. The bronze sample surface microstructure, achieved with SEM and EDX detector

In a previous paper, we have presented the behaviour in sea water of some shape memory copper alloys [28]. In this study, we have studied a tin bronze corrosion in seawater.

Experimental part

Materials and methods

A bronze sample was used. The chemical composition was determined using the spectrometer Metal Scan 2500. The chemical elements from the composition are presented in the table 1.

The chemical composition was determined by EDX analysis (VEGA II LSH, by Tescan Co. Czech Republic, coupled with the EDX QUANTAX QX2 detector) made by Bruker/Roentec Co., Germany). The results are presented in figure 2.

Corrosion environment

The corrosion environment is the Black Sea water with the composition (g . L⁻¹): Cl⁻ - 8.26; HCO₃⁻ - 0.183; CO₃⁻² - 0.022; SO₄⁻² - 1.137; Na⁺ - 4.47; K⁺ - 0.158; Ca²⁺ - 0.203; Mg²⁺ - 0.557, with the salinity of 15.0 g . L⁻¹.

Analysis method for the corrosion characteristics

For the chemical potential measurements we have used the VoltaLab PGP 201 (Radiometer Analytical SAS -Frana). For experimental data acquisition and processing, we have used the VoltaMaster 4 software. The corrosion tendency of a metal or alloy, which is immersed in an electrolytic medium, is determined based on the corrosion potential, $E_{\rm cor}$, which, in fact express the corrosion thermodynamically probability. This implies that at the metal/ solution interface the equilibrium is established for chemical oxidation-reduction reactions taking place on the surface. At the interface metal/solution there is a potential difference which, in the case when the electrochemical equilibrium is established, it is called *equilibrium potential* (\vec{E}_{a}) or *corrosion potential*. If there is no equilibrium (on the electrode surface occurs irreversible reactions), it is established so-called mixed potential or resting potential (E_m) . Both to the equilibrium potential electrodes and the mixed potential electrodes at metal / solution interface does not cross any macro current.

In order to assess the corrosion current value and corrosion rate respectively, has been used the *polarization resistance method*. The corrosion current determined by this method is the current that occurs at the interface of metal/corrosive environment when the metal is immersed in the solution, and represents the *instantaneous corrosion current*. From the practical point of view it is important to know the *instantaneously corrosion current density*, $(J_{corr}=I_{cor}/S)$, which is dependent by the *corrosion rate* (v_{corr}) .

 Table 1

 BRONZE CHEMICAL COMPOSITION

The working electrode, made from the studied material, was polished with sand paper SiC, up to 2000 grain size, degreased with acetone, washed with distilled water and placed in the electrochemical cell with the natural aerated seawater. It was used the standard measuring cell from the PG 201 facility, saturated calomel reference electrode and a platinum electrode as auxiliary electrode. The measurements were carried out at 25°C naturally aerated seawater.

The anodic polarization curves were recorded with a potential scan rate 0.5mV/s, with a potential range of ± 200 mV related to the open circuit potential. The corrosion potential ($E_{cor} \equiv E(I = 0)$), the Tafel slopes (b_a and b_c), polarization resistance, the instantaneously corrosion current density (j_{cor}), and the corrosion rate were assessed using specialized software VoltaMaster 4.

Results and discussions

Polarization curves

The linear polarization curves are shown in figure 3 using semi-logarithmic coordinates (Evans diagram) for the sample corroded in the naturally aerated Black Sea seawater.





Fig. 3. Evans diagram for the bronze sample in the Black Sea water

The parameters calculated based on these diagrams are shown in the figure basement and highlights the following:

- the corrosion potential, even though it is negative, it is shifted to more positive values than those found for the shape memory alloys, indicating a good corrosion resistance of this alloy;

- the cathodic process is controlled by diffusion; the cathodic sector slope from the polarization curve is steeper than the anode sector slope. Due to the diffusion process, despite the fact that the polarization resistance has a very small value the corrosion rates are 3...4 times smaller than the instantaneously corrosion for the shape memory alloys, which were previously studied in the same conditions [22, 28].

Cyclic polarization curves (fig. 4) recorded from a higher potential range can give additional information about the processes occurring into the system.

In the present study cyclicpotential diagrams (voltammograms) were recorded on the potential range (-1000... +1500... -1000) mV/ESC with a potential scan rate of 5 mV/s. Natural aeration was used to approach as much



Fig. 4. Electric potential voltammograms diagram for the bronze sample in the naturally aerated Black Sea water

as possible to the natural conditions. The tests started from a negative potential high enough to clean the surface by electrochemical reduction of all ionic or molecular species that may contaminate the surface of the alloy.

The following aspects may be highlighted:

- on the anodic sector two distinct maximal values are identified (A1 and A2), and on the (cathodic sector) just one single negative peak is identified (C). At the end of the anaodic sector, close to the 1V/ESC potential, can be observed a pronounced negative peak, which can be associated to the advanced electrochemical surface cleaning. After the anodic peaks, an almost horizontal plateau follows, corresponding to the surface passivation state;

- anodic peak A₁ is associated with the successive formation of the Cu₂O, CuO and Cu(OH)₂ compounds, the quantitative ratio between them, leads to both peak position and the current density value:

 $\begin{array}{ll} 2\text{Cu} + \text{H}_2\text{O} \leftrightarrow \text{Cu}_2\text{O} + 2\text{H}^+ + 2\text{e}^-\\ \text{Cu} + \text{H}_2\text{O} \leftrightarrow \text{CuO} + 2\text{H}^+ + 2\text{e}^-\\ \text{Cu}_2\text{O} + \text{H}_2\text{O} + 2\text{OH}^- \leftrightarrow 2\text{Cu(OH)}_2 + 2\text{e}^- \end{array}$

- in this potential domain, due to the high concentration of chloride ions, is possible to form CuCl or CuCl₂ chemical compounds, but also $(Cu_2Cl(OH)_3 [11] - according to the following chemical reactions:$

 $\begin{array}{l} Cu+Cl^{*}\rightarrow CuCl(s)+e^{*}\\ Cu+2Cl\rightarrow CuCl_{2}+2e^{*}\\ Cu_{2}O+Cl^{*}+2H_{2}O^{*}\rightarrow Cu_{2}Cl(OH)_{3}+H^{+}+2e^{*}\\ \end{array}$

- the second anodic peak (A2) can be associated with the transformation CuCl in CuO – according to the following reaction:

$$CuCl + H_{9}O \rightarrow CuO + Cl^{-} + 2H^{+} + 2e^{-}$$



Fig. 5. The metal surface image after cyclic polarization in the Black Sea water:(a) optical microscopy, (b) electronic microscopy

but also can be associated with the transformation Cu_2O in $Cu(OH)_{,r}$, followed by the Cu_2O_3 formation.

- on the cathodic sector, unlike the shape memory alloys, one single peak appears (C), which is associated with the Cu⁺ and Cu²⁺ reduction to metallic copper, regardless of the solid compound in the double layer formed during anodic processes.

Samples SEM analysis after cyclic polarization

Metallic copper crystallized by reducing copper oxides and hydroxides, it can be seen both in the optical photomicrographs of the surface and in the SEM micrograph (fig. 5).

The EDX microanalysis confirms the composition of the surface layer. An EDX line scan is shown in figure 6.

Analyzing the diagram it can be seen that Cl correlates with Sn, suggesting the presence of a compound Sn-Cl. Detailed studies of some copper alloy were made in two doctoral theses [27-29].

Corrosion over time for the bronze samples

Optic microscope analysis

The sample was immersed in a sealed tank containing water from the Black Sea. After 40 days the sample was removed from the solution, rinsed with distilled water, dried in air and the surface was examined under the optical microscope (Zeiss Axio Imager A1m). Images were analyzed both dark field (fig. 7) - which allows observation of the true natural colors of corrosion products, but also in bright field (fig. 8), which provides more details on the microstructure but the colors are altered due to the reflected rays reaching the observer. Visual examination of the sample surface after exposure to seawater shows a heterogeneous surface coated with blue-green compounds (fig. 8). It is obvious the occurrence of the corrosion products, but their nature can not be identified from these figures.

The qualitative information on the elements present on the surface was obtained from the EDX spectrums and revealed the presence of Cu, Sn, Al, S, Cl and O. In both cases the essential components are copper and oxygen, and tin, chlorine, sulfur and aluminum are present in a very small amount. It may be assumed that the prevailing



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Fig. 6. EDX line scan on the bronze sample surface after cyclic polarization in the Black Sea water



Fig. 7. Dark field optical micrographs of the sample kept 40 days in seawater: left - at 50X, right - at 100X.



Fig. 8. SEM images of the sample kept 40 days in seawater: left - at 500X, right - at 1000X

surface is civered with cuprous oxides and copper basic chloride, and the signal for the tin oxide is approximately the same as in the original alloy. It is likely that the absorbed aluminum comes from the seawater [27].

The experimental obtained data are consistent with the existing literature [27, 29]; the main corrosion products detected on the surface of the bronze alloy are copper basic chloride, and a mixture of copper and tin oxides.

Conclusions

Analysis of the corrosion products and corrosion parameters for tin bronze gives useful information in order to assess the behaviour in time, during service, under load, for the moving parts used in shipbuilding, made from the studied material.

It can be appreciated that tin bronze presents good corrosion resistance in seawater, respectively an adequate corrosion potential, due to the cathodic process which prevails. This means that the oxidation process is done by element diffusion.

The film oxides and chlorine-based complex compounds that occur after the immersion in seawater samples bronze is relatively compact, which indicates a corresponding resistance to corrosion in marine environment.

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