Research, Society and Development, v. 11, n. 12, e41111234104, 2022
(CC BY 4.0) | ISSN 2525-3409 | DOI: http://dx.doi.org/10.33448/rsd-v11i12.34104

Investigation of corrosive processes in the hull of a shipwreck in 1905

Investigação de processos corrosivos no casco de um navio naufragado em 1905

Investigación de procesos corrosivos en el casco de un naufragio en 1905

Received: 08/15/2022 | Reviewed: 08/26/2022 | Accept: 08/28/2022 | Published: 09/06/2022

Silvio Leonardo Valença
ORCID: https://orcid.org/0000-0002-3045-2732
Universidade Federal de Sergipe, Brasil
E-mail: silviovalenca@bol.com.br
Cochiran Pereira dos Santos
ORCID: https://orcid.org/0000-0001-9819-6002
Universidade Federal de Sergipe, Brasil
E-mail: cochiran@hotmail.com
Gabriela Oliveira Valença
ORCID: https://orcid.org/0000-0003-3863-5207
SergipeTec, Parque Tecnológico, Brasil
E-mail: gabriela.ovalenca@gmail.com
Orlando Pedreschi Neto
ORCID: https://orcid.org/0000-0002-1952-3712
Universidade Federal de Sergipe, Brasil
E-mail: opn1963@gmail.com

Abstract
This study presents the analysis and characterization of the corrosive process in the metallic material that makes up the hull of a shipwreck in 1905 in the Baia de Todos os Santos in the city of Salvador - Bahia - Brazil. Samples were collected from fragments of the shipwreck's hull by scuba diving. The results obtained through techniques such as electrochemistry and scanning electron microscopy, allowed the analysis of the process and products of corrosion in the metallurgical structure, as well as metallography to verify the phases present in its structure after the manufacturing process in the last century. The constitution of the Black Adder's hull, built in 1869, consists of a low carbon steel alloy, containing high levels of impurities, mainly phosphorus and sulfur, demonstrating the low metallurgical quality of the time.
Keywords: Corrosion; Metal alloys; Black adder.

Resumo
Esse estudo apresenta a análise e caracterização do processo corrosivo no material metálico que compõe o casco de um navio naufragado no ano de 1905 na Baía de Todos os Santos da cidade de Salvador - Bahia - Brasil. As amostras foram coletadas de fragmentos do casco do naufrágio por mergulho autônomo. Os resultados obtidos por meio de técnicas como a eletroquímica e microscopia eletrônica de varredura, permitiram a análise do processo e produtos da corrosão na estrutura metalúrgica, como também da metalografia para constatar as fases presentes na sua estrutura após o processo de fabricação no século passado. A constituição do casco do navio Black Adder construído em 1869, consiste em uma liga de aço baixo carbono, contendo elevados teores de impurezas, principalmente fósforo e enxofre, demonstrando a baixa qualidade metalúrgica da época.
Palavras-chave: Corrosão; Ligas metálicas; Black adder.

Resumen
Este estudio presenta el análisis y caracterización del proceso corrosivo en el material metálico que conforma el casco de un barco naufragado en 1905 en la Bahía de Todos os Santos en la ciudad de Salvador - Bahía - Brasil. Se recolectaron muestras de fragmentos del casco del naufragio mediante buceo. Los resultados obtenidos a través de técnicas como la electroquímica y microscopía electrónica de barrido permitieron el análisis del proceso y productos de corrosión en la estructura metalúrgica, así como la metalografía para verificar las fases presentes en su estructura luego del proceso de fabricación en el siglo pasado. La constitución del casco del barco Black Adder, construido en 1869, consiste en una aleación de acero de bajo carbono, que contiene altos niveles de impurezas, principalmente fósforo y azufre, lo que demuestra la baja calidad metalúrgica de la época.
Palabras clave: Corrosión; Aleaciones metálicas; Black adder.

1. Introduction

Ferrous metallic structures immersed in marine environments are constantly prone to participate in the chemical processes of corrosion and concretion during their lifetime. Corrosion processes of ferrous alloys in marine environments, as well as the colonization of encrusting organisms, promote the encapsulation of the metal by these organisms, distancing it from dissolved oxygen, promoting a rapid stabilization of metallic structures of shipwrecks in tropical waters (Bekić et al., 2011; McLeod, 2011). However, despite these processes being representative in the maintenance of archaeological material, it is still poorly studied in tropical waters (McLeod, 2016).

The concretion is formed by products resulting from the corrosion of metallic structures and the marine environment, such as the presence of microorganisms (Zhang, 2014) and hydrological parameters such as pH, among others (McLeod, 2016). The concretion process starts with the colonization of a free surface by pioneer species such as bacteria, protozoa, microalgae and macroalgae that form a biofilm on the surface of the shipwreck (Bekić et al., 2011). This biofilm then provides a source of nutrients and makes the substrate favorable for the colonization of macroorganisms, forming a complex layer of organisms composed of macroalgae, sponges, cnidarians, bivalves, tubercular polychaetes, cirripedians, bryozoans and tunicates (Bekić et al., 2011; GISP, 2008; Messano, 2008). This colonization process can be intensified with the iron content present in the metal alloy (McLeod, 2016), because it is a limited chemical element in marine environments and fundamental for several cellular metabolic processes (Zhang, 2014).

The study was carried out at Praia da Boa Viagem, Baia de Todos os Santos, in the municipality of Salvador, Bahia, Brazil, at coordinates 12° 30.108’ S and 38° 30.678’ W (Cirano, 2007). In this area between the 8 to 15 m isobaths, the Black Adder sank in 1905 (Lubbock, 1914; Pedreschi, 2020).

The Black Adder was launched on February 1, 1870, at Greenwich, by Maudslay, et al., The ship measured 66.0 m long, 10.7 m wide, weighing 917 tons. The Black Adder is a clipper, a class of large craft with a long narrow hull, large masts and a large sail area. These vessels had a large draft, with thin shapes at the front and tapered stern, reconciling speed with the ability to carry large loads on the main routes of maritime navigation. They were normally armed with three masts and had their development from the beginning of the 19th century, reaching their apogee in the middle of the second half of this century, extending until the end of the 1870s, when regular steam navigation and opening of the Suez Canal began to hamper the traffic of this type of vessel (Mantuano, 2017).

Archeology is a multidisciplinary science that aims to reconstruct the cultural processes of the past from the analysis of material culture (Rambelli, 2016). Through the study of these materials, when related to studies of similar cultures and ecological variables, one can better understand the past of human activities. In the case of archaeometallurgy, which is an area of archeology dedicated to the study of metallic artifacts, techniques widely applied in science are used (Artioli, 2012).

Metallurgical technology has been a field of interest for archeology since instrumental analytical methods were initiated and developed. In the traditional evolutionary explanation of history, technology has played a fundamental role of reference (Tylecote, 2002). Technological advances and improvements are associated with social and economic changes and advances. The metal, as a technology developed from Prehistory, acquires an informative value of reference and its study was guided mainly by the growing demand during much of the 20th century, being based on the elemental analysis, mainly of the objects obtained from it (Artioli, 2012).

In electrochemical corrosion tests, it is very common to use experimental polarization curves to determine the corrosion rates of metal/electrolyte systems. Many commercial equipment comes with specific software that determines the values of Tafel constants directly from experimental polarization curves, using portions of the curve for high potential values. These also determine the value of the polarization resistance obtained from the linear stretch of the experimental curves. Using these three parameters, this equipment estimates the values of the corrosion rates of the studied systems. This procedure is based on the Butler-Volmer equations that represent electrochemical systems in equilibrium governed by activation polarization.

Currently, several techniques are available for studying metals, for characterization and mechanical tests such as optical emission spectrometry, microhardness, scanning electron microscopy and mechanical tests of traction, bending and impact, among others. The optical emission spectrometry technique was used in this research to determine the chemical composition together with the corrosion electrochemistry experiment, objectives of this study.

2. Methodology

The samples were obtained from the collection of fragments of the wreck's hull by scuba diving. In the laboratory, concretion was removed from the surfaces of the metal fragments by mechanical pickling. Then, the samples were cut by an abrasive disc, in the dimensions of 60.0 x 40.0 x 3.0 mm in thickness and their surfaces were flattened through the manual sanding process, and the sample that presented the best characteristics for analysis can be seen in Figure 1.

Figure 1: Fragment sample of the wreck's hull prepared for analysis.

Source: Authors.

Chemical analysis of the hull sample was performed using optical emission spectrometry (Oxford Foundry-Master Xpert). The sample was embedded in thermoset resin (Bakelite), sanded and polished with diamond paste from 6 to 1 μm. The etching to reveal the microstructure was carried out using the 2% Nital reagent (2 ml of HNO_3 + 98 ml of ethyl alcohol). The images of the metallographs were obtained using an optical microscope (Leica DM2500).

The electrolytic solution used in the electrochemical corrosion tests was sea water synthesized at the Corrosion and Nanotechnology Laboratory (LCNT/NUPEG/UFS) in accordance with the current standard of the American Society for Testing and Materials (ASTM D 1141-98).

To obtain the electrochemical analyses, the tests were carried out in a potentiostat/galvanostat (PGSTAT 302) at room temperature, in a 250 ml cell using a fixed volume of 80 ml solution and three electrodes: reference electrode (silver wire), counter electrode (platinum wire) and the working electrode with an exposed surface area of 1.0 cm².

All steel samples from the ship's hull initially underwent zero current conditioning ($i = 0$) at the Open Circuit Potential (OCP) during the stabilization time of 1200 seconds. This procedure served to obtain an estimated corrosion potential of the metal so that it was possible to obtain the variation of potential applied by the equipment to obtain the experimental polarization curve.

The current applied to the electrode was controlled by the potentiostat/galvanostat, allowing the measurement of the electrical potential difference between the working and reference electrodes with a sweep speed of 1 mV/s and ± 300 mV of the OCP. The results of the corrosion rate of the metallic material of the ship's hull were analyzed in ANOVA 2.1.5 and Origin 2016 software for interpretation and plotting of graphs and results.

Scanning electron microscopy is a method of obtaining images of the microstructure and morphology of materials. A high-energy electron beam is focused on the material and sweeps across the surface, where different interactions between the electron beam and the material occur, leading to the emission of photons and electrons from the surface (Chirikure, 2014). The scanning electron microscopy images were obtained from the material samples of the ship's hull after the electrochemical corrosion process, through a JEOL microscope, model JSM-6500 LV, at the UFS Multiuser Nanotechnology Center (CMNano-UFS). The equipment was operated under vacuum and with an electron beam acceleration of 15 kV.

3. Results and Discussion

3.1 Chemical composition, microstructure and microhardness

The chemical analysis showed that the material that made up the hull of the Black Adder clipper, built in 1869 in London and wrecked in 1905 in Salvador, consists of a low carbon steel alloy (0.02%), still containing high levels of impurities, mainly phosphorus (0.34%) and sulfur (0.04%), according to Table 1.

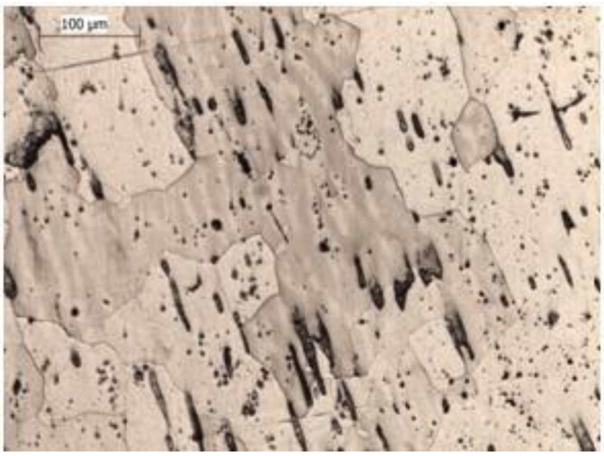
Table 1: Chemical analysis of the sample (% by weight).

Elements	C	Si	P	S
(%)	0.02	0.28	0.34	0.04

Source: Authors.

The low metallurgical quality is reflected in the microstructure consisting of coarse ferrite grains and a large number of inclusions (Figure 2), impairing the performance of the alloy's mechanical properties, causing low fracture toughness, low impact energy, among other mechanical properties of steel (Tylecote, 2002; Pedreschi, 2020). The microstructural heterogeneity also favors galvanic corrosion processes (Chirikure, 2014).

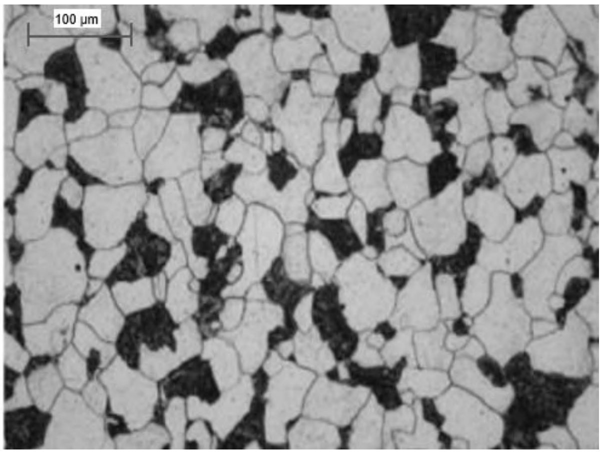
Figure 2: Microstructure of the sample showing formation of ferrite grains and large amount of elongated non-metallic inclusions.



Source: Authors.

It can be seen that the quality in relation to the chemical composition and mechanical properties of the metallic material used in the vessel is much lower than the current ones, such as the ASTM A131 steel (Gentil, 2011) used in the structural construction of the hull of ships, in which it has values with maximum chemical percentages of 0.180 (C), 0.500 (Si), 0.035 (P) and 0.035 (S). For comparison, Figure 3 shows the microstructure of a current low carbon ferritic steel alloy (ASTM, 2014).

Figure 3: Microstructure of a current steel profile sample, with formation of ferrite grains.



Source: Authors.

3.2 Determination of Tafel curves

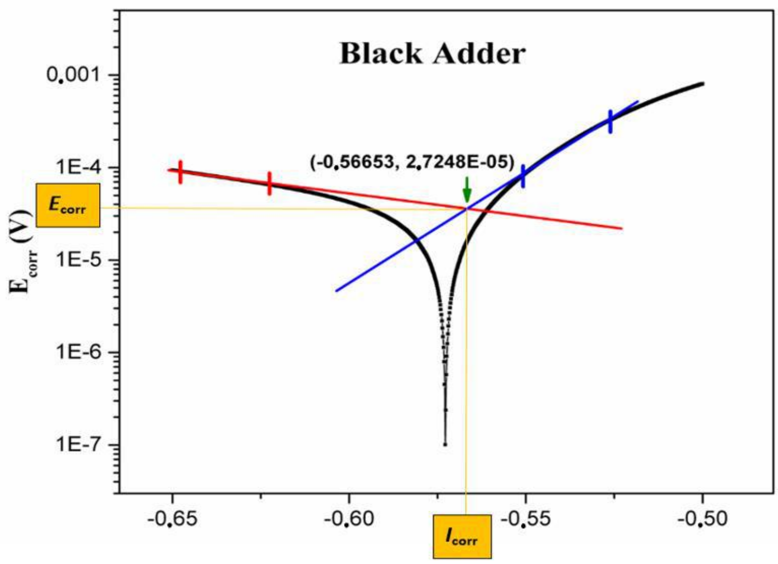
The measurement of electrochemical potential is a fundamental operation for determining the potential of a structure in relation to the environment, in order to assess the condition of the metallic material, that is, to verify if there is corrosion, if the structure is protected or if there is influence of interference currents.

Polarization curves can provide important information about the intensity and morphology of the processes that occur at the metal-solution interface. The applied potential corresponds to an activation energy and the current response indicates the speed of electrochemical processes that can be anodic or cathodic. The referred models of polarization curves are obtained with the pairs of points (log (|I|), E) and, for each applied electrode potential (E), the total current (I) is obtained by adding the currents anodic (positive) and cathodic (negative) currents of each of the reactions that occur at the interface of the considered system.

The polarization of an electrode by means of a potentiostat allows the creation of a polarization curve that is no longer representative of the polarization of a single reaction, but rather of the global effect of all reactions that occur simultaneously on the electrode (Omidi, 2017).

For the investigation of corrosive processes and the evaluation of corrosion protection systems, obtaining experimental polarization curves can be extremely valuable. Through the polarization curves, shown in Figure 4, it is possible to obtain several electrochemical parameters, such as the rate, potential (E_{corr}) and corrosion current (I_{corr}), as well as the Tafel slopes. In this way, the corrosion potential and the corrosion current were obtained through the intersection point of the lines, where a potential value close to zero was found, meaning that the material of the ship's hull has low corrosion resistance (Wolynec, 2003).

Figure 4: Tafel curves with their extrapolations.



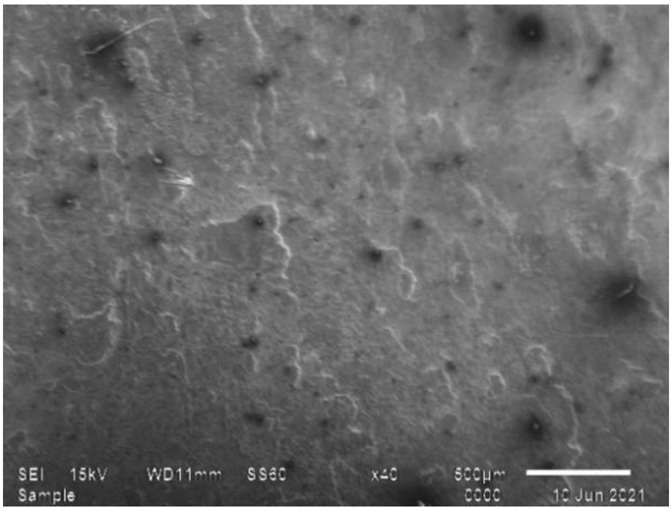
Source: Authors.

3.3 Scanning Electron Microscopy (SEM)

In Figures 5, 6 and 7, pitting corrosion is observed on the surface of the material, which is an extremely localized form of corrosion that leads to the generation of small holes in the metal. In turn, an electrochemical reaction occurs within the cavity of the material, which is accelerated by the presence of halides, mainly chlorides, with a local increase in acidity (concentration of H+).

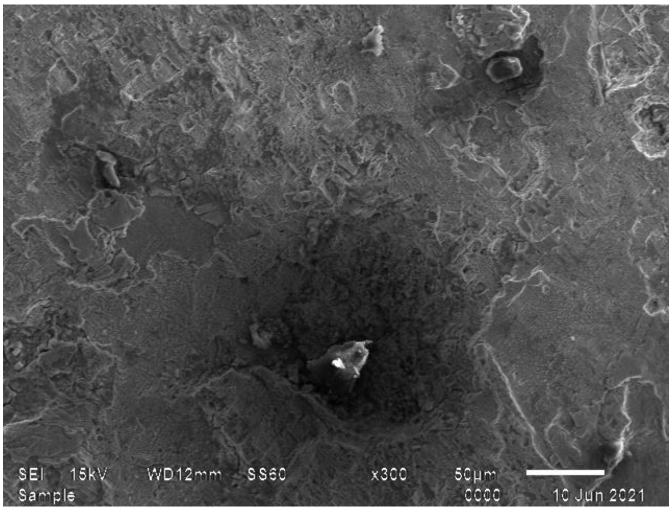
The pitting corrosion process is accelerated due to a relationship between extremely unfavorable anodic areas, that is, a small anodic area where corrosion occurs and a large cathodic area where there is electron consumption and oxygen evolution, in aqueous media, such as in the experiment with synthesized seawater.

Figure 5: Scanning Electron Microscopy image at 40x, showing the morphology of the sample.



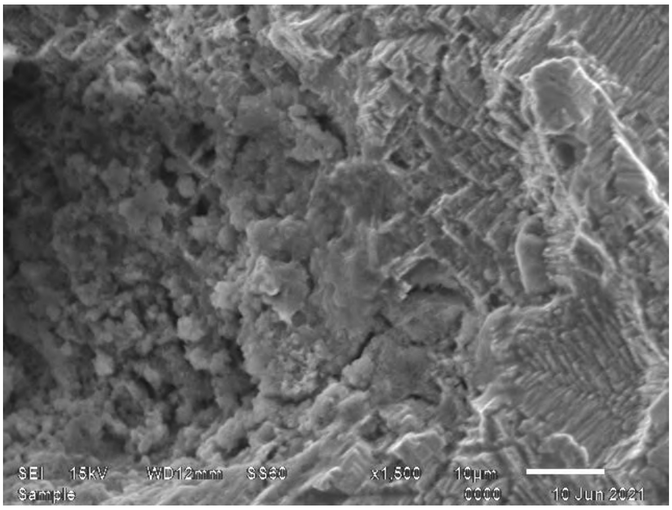
Source: Authors.

Figure 6: Scanning Electron Microscopy image at 300x, showing the formation of pitting corrosion.



Source: Authors.

Figure 7: Scanning Electron Microscopy image at 1,500x, in which the electrochemical reaction located inside the cavity of the material is noted.



Source: Authors.

4. Conclusion

It is clear that the structural metallic materials used in the last century for the construction of ship hulls did not have manufacturing processes and quality controls of high performance in relation to their chemical compositions, manufacturing processes and mechanical properties, when compared to steels structures currently manufactured.

Regarding the corrosion resistance of the metallic material of the ship's hull, it was observed that it has a metallurgical structure with low resistance to the corrosive process, as can be seen in the scanning electron microscopy images. This is certainly a consequence of the lack of alloying elements present in its chemical composition, such as nickel, and the high percentage of chemical elements such as phosphorus and sulfur in its composition.

(CC BY 4.0) | ISSN 2525-3409 | DOI: http://dx.doi.org/10.33448/rsd-v11i12.34104

Finally, the aspect of product improvement, when compared through archaeometallurgy and current metallurgy, is certainly associated with scientific and technological advances, as well as with the emergence and improvement of techniques and equipment to obtain improvements in materials and the development of new materials.

Acknowledgments

The authors are grateful for the use of the DFI/UFS, DCEM/UFS, CLQM/UFS, LCNT/NUPEG/UFS laboratories. This research used facilities of the Multiuser Centre for Nanotechnology of UFS (CMNano-UFS), a non-profit organization member of the National Multiuser Centres sponsored by Financiadora de Estudos e Projetos (FINEP). The CMNano technical staff is acknowledged for the assistance during the experiments under the proposal number [#047/2021].

References

Bekić, L., Ćurković, M., Jelić, A., Jozić, A., Mustaček, M., Perin, T., & Pešić, M. (2011). *Conservation of underwater archaeological finds - Manual*. International Centre for Underwater Archaeology in Zadar. 94p.

McLeod, I. D., & Vicki, L. R. (2011). *In situ conservation surveys of iron shipwrecks in Chuuk Lagoon and the impact of human intervention*. AICCM (Australian Institute for the Conservation of Cultural Materials) Bulletin Volume 32.

McLeod, I. D. (2016). *In situ* corrosion measurements of WWII shipwrecks in Chuuk Lagoon, quantification of decay mechanisms and rates of deterioration. *Frontiers in marine science*. 3. Article 38.

Zhang, Z., Ma, Q., Li, N., & Tian, X. (2014). *Research on the removal of calcareous and iron concretions from marine finds*. Proceedings of the 2014 Asia-Pacific Regional Conference on Underwater Cultural Heritage. Dublin.

GISP (Global Invasive Species Programme). (2008). *Marine Biofouling: An Assessment of the Risks and Management Initiatives*. Compiled by Lynn Jackson on behalf of the Global Invasive Species Programme and the UNEP Regional Seas Programme. 68pp.

Messano, L. V. R., Sathler, L., Reznik, L. Y., & Coutinho, R. (2008). *Biocorrosão marinha: interface entre a bioincrustação, processos eletroquímicos e ciência dos materiais*. Revista Pesquisa Naval, 21, p. 32-43. Brasília.

Cirano, M., & Lessa, G. C. (2007). Oceanographic characteristic of Baia de todos os Santos. *Brazil. Rev. Bras. Geof*. 25. 363-387.

Lubbock, B. *The China Clippers*. (1914). (2ª ed.) Glasgow: James Brow & Son Publishers.

Pedreschi, O., Santos, C. P., Valença, S. L., Griza, S., Sussuchi, E. M., & Valença, G. O. (2020). Análise e caracterização do casco de um navio naufragado na Baia de Todos os Santos - Bahia – Brasil / Analysis and characterization of the hull of a shipwrecked ship in the Baia de Todos os Santos - Bahia - Brazil. *Brazilian Journal of Development*, *6*(10), 83933–83942. https://doi.org/10.34117/bjdv6n10-726

Mantuano, T. V. (2017). *A Revolução dos Vapores na Navegação Marítima*. XII Congresso Brasileiro de História Econômica & 13ª Conferência Internacional de História de Empresas. Rio de Janeiro.

Rambelli, G. (2016). *Arqueologia subaquática em Cananéia*. Ed. Prismas. 240p.

Artioli, G. (2012). *Archaeometallurgy: the contribution of mineralogy*. Congreso SEM-SEA. International Seminar. Archaeometry and Cultural Heritage. Bilbao, Espana.

Tylecote, R. F. (2002). *A history of metallurgy*. Ed. Institute of Materials. (2ª ed.). 205p.

Chirikure, S. (2014). *Geochemistry of Ancient Metallurgy: Examples from Africa and Elsewhere*. University of Cape Town. Treatise on Geochemistry. (2nd Edition.) Ed. Elsevier.

Gentil, V. *Corrosão*. (2011). (6ª ed.). Editora LTC.

ASTM A131/131M-14. (2014). Standard Specification for Structural Steel for Ships.

Griza, S., Martins, D. A., Silva, A. A., & Reis, R. C. S. (2015). *Análise de falhas em perfil utilizado na construção civil*. 70º Congresso da ABM.

Smart, N. R., & Adams R. (2006). *Natural analogues for expansion due to the anaerobic corrosion of ferrous materials*. Technical Report. Swedish Nuclear Fueland Waste Management Co. Sweden.

Omidi, M., Fatehinya, A., Farahani, M., Akbari, Z., Shahmoradi, S., Yazdian, F., Tahriri, M., Moharamzadeh, K., Tayebi, L., & Vashaee, D. (2017). Characterization of Biomaterials. In *Biomaterials for Oral and Dental Tissue Engineering*; Elsevier, 97-115.

Wolynec, S. (2003). *Técnicas eletroquímicas em corrosão*. (Ed. 49). Ed. Universidade de São Paulo, 184p.