STUDY REGARDING THE INFLUENCE OF CORROSIVE AGENTS ON THE SURFACE OF METALLIC MATERIAL LIKE STEEL

OLGA POPA¹, ANDREI-VLAD CIUBOTARIU¹, COSMIN CONSTANTIN GRIGORAS¹, ANA-MARIA ROSU^{2*}, VALENTIN ZICHIL¹

¹Department of Engineering and Management, Mechatronics, "Vasile Alecsandri" University of Bacau, Calea Marasesti 157, Bacau, 600115, Romania

²Department of Chemical and Food Engineering, "Vasile Alecsandri" University of Bacau, Calea Marasesti 157, Bacau, 600115, Romania

Abstract: Corrosion is a process that involves the action of different agents on material surfaces. Corrosive agents in corrosion field can be ambient, saline and microbiological mediums. These agents can influence the mechanical properties of metallic material like steel. The aim of this research is to present the mechanic properties of sheet steel submitted at the action of corrosive agents. The metallic samples were analyzed in order to determinate the resistance at corrosion by stress-strain curves, deformation limit curves and (Atomic Force microscopy) AFM images. Relative results are obtained in the case of saline medium corrosion, meaning that the saline medium corrosion influences the metallic sample, in proportion to the degree of salinity. Also, the AFM images and topographies of metallic surface confirm this conclusion.

Keywords: saline corrosion, microbiological corrosion, sheet steel, mechanic properties, AFM images

1. INTRODUCTION

Corrosion is a damaging attack on metals surfaces that results in negative effects. Metallic materials can be exposed to different environments, when they can be corroded by several agents. Various environmental factors affect the chemical composition of metallic materials. The environmental factors can be: water, air and microorganisms, electrochemistry process, etc. [1-4].

Electrochemical processes are the base processes of metallic materials corrosion. The metallic atoms tend to pass in corrosion solution like ions. Thus, in the corrosion process are three essential components resulted: the anode parte, based on the location of the metal under corrosion; the electrolyte part described by the corrosive medium and the cathode part based on the electrical conductor that remains unconsumed during corrosion process [5-9].

When microorganisms act on metallic surfaces it is formed a biofilm. The biofilm is produced by bacteria, if the medium is favorable to develop them [5, 6]. In biofilm bacteria occur distinct physiological characteristics like resistance to antibiotics, increased production of exopolysaccharide, changes in unicellular morphology and different responses to environmental stimuli [9-11].

The attack over metallic materials by fungus is explained by the fact that from fungus metabolism a lot of organic acids, like tartric, citric and oxalic acid, solubilize the metals [12-19]. The corrosive action of fungus

^{*}Corresponding author, email: <u>ana.rosu@ub.ro</u>

^{© 2022} Alma Mater Publishing House

over metal material is accentuated in warm and humid areas where damages are very important [20-24]. The species of fungus which attack metallic materials and plastic materials are: *Trichoderma*, *Neurospora*, *Fusarium* sp., *Aspergillus* sp., *Penicillium* sp., *Chaetomium* and *Sterigmatocystis* [21-24].

Biodegradation is a naturally occurring process in a polluted environment where microorganisms are present [22, 23]. Biocorrosion is a significant factor in the increases in the process and repairs cost in industries [25-27].

There is organic compound that exists in the structure of vegetable extracts which can be divided into hydrophobic and hydrophilic compounds [18-22]. Hydrophobic compounds provide protection from the metallic surface while the hydrophilic compounds prevent corrosion by being adsorbed on the surface and constructing a biofilm [28, 29]. Studies reached 68% and 45% protection degrees for steel in a saline electrolyte in the presence of the aqueous extract of vegetables [30-32]. Therefore, as can be perceived, these inhibitors have low inhibition performance in saline solutions. One way to promote the efficiency of these inhibitors is the application of heavy metallic species such as zinc cations [33].

In present experimental study, metallic material, like steel, is use in contact with corrosive agents such as: ambient (chemical laboratory conditions), saline (7% and 11%) and microbiologic (bacteria and fungus) mediums. The contact with agents influences the mechanical properties of metallic material and the resistance of the metallic material at mechanic processing. All these properties were tested by stress-strain curves, deformation limit curves and AFM images and topographies.

2. EXPERIMENTAL CONDITIONS

2.1. Metallic materials description

General characteristics of chemical composition and dimensions of metallic material sample use, steel, are presented in Table 1 and Table 2.

Table 1. Chemical composition of steel as metalic material (76).													
Steel	Si	Fe	Cu	Mn	Cr	Ni	Al	С	Р	S	N_2	Mo	As
	0.02	99.614	0.02	0.23	0.02	0.01	0.035	0.03	0.009	0.006	0.004	0.001	0.001

Table 1. Chemical composition of steel as metallic material (%).

Table 2. Size of the metallic material.

Metallic material	Length, cm	Width, cm		
Steel	20	1.8		

2.2. Corrosives agents

Steel samples were used and submitted to different corrosive medium for 30 days at room temperature. Corrosives agents were ambient conditions that exist in a chemistry laboratory at room temperature, saline and microbiological medium.

As a blank sample it has been used distilled water as a corrosive agent. For the action of the saline medium, different concentrations of sodium chloride (NaCl) were used: 7 and 11% respectively.

As microbiological corrosive agent it has been used microbiological medium, where different types of microorganisms are developed. Malt yeast extract agar (MYEA) medium was prepared as follows: 2.0% malt extract, 0.2% yeast extract and 1.5% agar in distilled water.

All compounds were diluted in distilled water, sterilized at 120°C for 120 minutes. After sterilization, microbiological medium is preserved at room temperature for an optimum distribution of temperature. Metallic samples are introduced in a noted tube with microbiological medium, and inoculated with different types of microorganisms that can be presented in an industrial hall. The types of microorganisms presented belong to the fungus and mould type.

2.3. Experiments equipment

Determination of mechanical properties was realized by a trenching test carried on a universal tensile testing machine, EZ50 (tensile force 50kN), at deforming speed 10 mm/min. The measurement of the specific deformations needed for the stress-train diagram was accomplished with two EPSILON mono-axial

extensometers. The interesting mechanic parameters were: yield strength (MPa), total elongation (%), anisotropy factor and hardening factor.

Images of the metallic material surface were tested with Atomic Force microscopy (AFM), A.P.E. Research model A100 which permits a resolution of 0.02 nm.

3. RESULTS AND DISCUSSIONS

The samples were corroded for 30 days by the corrosive agents and at the final time the metallic samples were taken out from corrosive medium and submitted to the determination of mechanical properties.

In Table 3 are presented the mechanical properties of the steel samples determined by experimental tests for the action of each corrosive medium.

Table 5. Mechanic properties of steel samples.								
Sample	Corrosive Ag	gents	Limit strength [MPa]	The total elongation, [%]	Anisotropy factor, r	Hardening factor, n		
	Environme	ent	260.71	43.1	2.5842	0.1944		
	Saline	Blank	267.82	42.1	1.9871	0.1708		
		7%	272.47	28.5	2.26127	0.1392		
Steel		11%	268.18	22	2.10709	0.1575		
		Blank	254.29	18	1.81665	0.1669		
	Microbiological	Fungus	279.57	20	1.89406	0.1636		
		Mould	268.67	21	2.11241	0.1681		

Table 3. Mechanic properties of steel samples

In Figure 1 is presented the stress-strain diagram for the steel sample obtained after saline medium action (water, 7% NaCl and 11% NaCl concentration) compared with the action of the ambient medium.



Fig. 1. Stress-strain curves for steel sample in the saline medium compared with the ambient medium.

According to the diagram, it can be observed differences in curve levels for the action of corrosive agents. At 7% and 11% NaCl concentrations can be distinguished that the corrosive effects of the mechanical properties are influenced by increased concentration of the saline medium. At 11% saline concentration, the metallic sample suffer a faster breakage compared to the 7% saline and ambient medium. This less resistance at real stress is due to significant NaCl crystals present at the material surface.



Fig. 2. Stress-strain curves for steel sample in microbiological medium compared with ambient medium.

The action of microbiological agents, presented in Figure 2, is due to the low level of the stress-strain curve comparatively with the level of the curve in the case of the ambient medium action. Microorganisms synthesized compounds that produce a low resistance to corrosion.

Figure 3 and Figure 4 present the AFM images and topographies of the metallic sample after the action of ambient and saline medium (7% NaCl concentration). The topography presents the texture, waviness and roughness of the analyzed sample at AFM microscope. After topography analyzes, it can be remarked pitting corrosion in the case of the action of 7% NaCl solution.



Fig. 3. AFM images and topography of steel sample after ambient medium action.



Fig. 4. AFM images and topography of steel sample after 7% NaCl solution action.

As a result of the action of 11% NaCl solution, in AFM images and topographies of metallic material (Figure 5), can be observed higher levels of unevenness comparatively with the action of 7% NaCl solution. The result is explained to the formation of carbonated compounds in contact with a metallic material.

The micro-pitting encouraged by microorganism strains looks different in comparison with the ambient control system, as revealed by the standard AFM software on the pitted areas. Figures 6, 7 and 8 present AFM images and topography of steel samples after microbiological medium action.



Fig. 5. AFM images and topography of steel sample after 11% NaCl solution action.

It analyzed the action of fungus and mould type of microorganisms, which are present in an industrial hall. From the presented topographies can be observed that the actions of mould and fungus types on the metallic material are manifested by the formation of rare but deep asperities. This significant result is due to the microorganism spore's presence that can attack metallic surfaces.



Fig. 6. AFM images and topography of steel sample after microbiological blank action.



Fig. 7. AFM images and topography of steel sample after microbiological fungus agent action.



Fig. 8. AFM images and topography of steel sample after microbiological mould agent action.

Microbiologically influenced corrosion processes start with biofilm formation on the metal substrate. Texture, waviness and roughness parameters are important to explain the action of corrosive agents on metallic materials.

4. CONCLUSIONS

Saline corrosive medium from 0.85% NaCl in distillated water to 11% NaCl in saline medium tested provide that a higher saline concentration corrodes metallic materials. The inhibitor effect can occur due to limestone and carbonate deposit on study sample.

The corrosion resistance at the action of corrosive agents on metallic material, like steel, is based on the formation of a passive biofilm on the surface of the material. This biofilm is provided by the presence of metal-hydrate oxide formatted, which can influence the corrosion resistance. Biofilm formation assisted pit formation on the carbon steel surface and it was evidenced by the AFM analysis. Corrosion current was increased in the presence of corrosion agents, this observation confirmed that microorganisms and salinity play key role in the corrosion of carbon steel.

In conclusion, this experimental study presents the electrochemical process that results after the action of different corrosion agents on steel as metallic material.

REFERENCES

[1] Jiayue, Z., Laszlo, C., Geoffrey, M., Biocorrosion of copper metal by *Aspergillus niger*, International Biodeterioration and Biodegradation, vol. 154, 2020, p. 105081.

[2] Tingyue, G., Di, W., Yassir, L., Dake, X., Extracellular electron transfer in microbial biocorrosion, Current Opinion in Electrochemistry, vol. 29, 2021, p. 100763.

[3] Hussein, M.A., Ankah, N.K., Madhan, A., Kumar, Azeem, M.A., Saravanan, S., Sorour, A.A., Aqeeli, N.Al., Mechanical, biocorrosion, and antibacterial properties of nanocrystalline TiN coating for orthopedic applications, Ceramics International, vol. 46, no. 11, part B, 2020, p. 18573-18583.

[4] Noyel, S.V., Sharma, A., Manivannan, R., Metal corrosion induced by microbial activity – mechanism and control options, Journal of the Indian Chemical Society, vol. 98, no. 6, 2021, p. 100083.

[5] Humayun, K., Khurram, M., Cuie, W., Yuncang, Li., Recent research and progress of biodegradable zinc alloys and composites for biomedical applications: biomechanical and biocorrosion perspectives, Bioactive Materials, vol. 6, no. 3, 2021, p. 836-879.

[6] Yuqiao, D., Yassir, L., Zhong, L., Dake, X., Soumya, E., Abed, S., Ibnsouda, K., Fuhui, W., Microbiologically influenced corrosion of 304L stainless steel caused by an alga associated bacterium *Halomonas titanicae*, Journal of Materials Science and Technology, vol. 37, 2020, p. 200-206.

[7] Aeshah, H.A., Localized corrosion and mitigation approach of steel materials used in oil and gas pipelines – an overview, Engineering Failure Analysis, vol. 116, 2020, p. 104735.

[8] Oulfat, A.A., Aragon, E., Fahs, A., Davidson, S., Ollivier, B., Hirschler-Rea, A., Iron corrosion induced by the hyperthermophilic sulfate-reducing archaeon *Archaeoglobus fulgidus* at 70 °C, International Biodeterioration and Biodegradation, vol. 154, 2020, p. 105056.

[9] Sachan, R., Singh, A.K., Comparison of microbial influenced corrosion in presence of iron oxidizing bacteria (*strains DASEWM1 and DASEWM2*), Construction and Building Materials, vol. 256, 2020, p. 119438.

[10] Jayasathyakawin, S., Ravichandran, M., Baskar, N., Anand Chairman, C., Balasundaram, R., Mechanical properties and applications of magnesium alloy – review, Materials Today: Proceedings, vol. 27, part 2, 2020, p. 909-913.

[11] Fayyad, E.M., Rasheed, P.A., Al-Qahtani, N., Abdullah, A.M., Hamdy, F., Sharaf, M.A., Hassan, M.K., Mahmoud, K.A., Mohamed, A.M., Jarjoura, G., Farhat, Z., Microbiologically-influenced corrosion of the electroless-deposited NiP-TiNi – Coating, Arabian Journal of Chemistry, vol. 14, no. 12, 2021, p. 103445.

[12] Ruiqiu, L., Qiang, L., Changkun, C., Hui, S., Siqi, L., Yijing, L., Zhongzhi, Z., Shanshan, S., Biocompetitive exclusion of sulfate-reducing bacteria and its anticorrosion property, Journal of Petroleum Science and Engineering, vol. 194, 2020, p. 107480.

[13] Yunting, G., Siqi, J., Lu, Q., Yingchao, S., Rui, G., Guangyu, L., Jianshe, L., Enhanced corrosion resistance and biocompatibility of polydopamine/dicalcium phosphate dihydrate/collagen composite coating on magnesium alloy for orthopedic applications, Journal of Alloys and Compounds, vol. 817, 2020, p. 152782.

[14] Little, B.J., Blackwood, D.J., Hinks, J., Lauro, F.M., Marsili, E., Okamoto, A., Rice, S.A., Wade, S.A., Flemming, H.-C., Microbially influenced corrosion-any progress?, Corrosion Science, vol. 170, 2020, p. 108641.
[15] Martynenko, N., Anisimova, N., Kiselevskiy, M., Tabachkova, N., Temralieva, D., Prosvirnin, D., Terentiev, V., Koltygin, A., Belov, V., Morosov, M., Yusupov, V., Dobatkin, S., Estrin, Y., Structure, mechanical characteristics, biodegradation, and in vitro cytotoxicity of magnesium alloy ZX11 processed by rotary swaging, Journal of Magnesium and Alloys, vol. 8, no. 4, 2020, p. 1038-1046.

[16] Harshal, M., Gurpreet, K., Ganga Ram, C., Nirmal, P., Assessment of bio-corrosion inhibition ability of Hafnium based cationic metallo-surfactant on iron surface, Corrosion Science, vol. 179, 2021, p. 109101.

[17] Taleb-Berrouane, M., Khan, F., Hawboldt, K., Corrosion risk assessment using adaptive bow-tie (ABT) analysis, Reliability Engineering and System Safety, vol. 214, 2021, p. 107731.

[18] Rodrigues, J.S., Antonini, L.M., Cunha Bastos, A.A., Zhou, J., Malfatti, C.F., Corrosion resistance and tribological behavior of ZK30 magnesium alloy coated by plasma electrolytic oxidation, Surface and Coatings Technology, vol. 410, 2021, p. 126983.

[19] Yazdi, M., Khan, F., Abbassi, R., Microbiologically influenced corrosion (MIC) management using Bayesian inference, Ocean Engineering, vol. 226, 2021, p. 108852.

[20] Pan, Y., Chaofang, D., Kui, X., Xiaogang, L., Study on corrosion behavior of β -Sn and intermetallic compounds phases in SAC305 alloy by in-situ EC-AFM and first-principles calculation, Corrosion Science, vol. 181, 2021, p. 109244.

[21] Dworschak, D., Brunnhofer, C., Valtiner, M., Complementary electrochemical ICP-MS flow cell and in-situ AFM study of the anodic desorption of molecular adhesion promotors, Applied Surface Science, vol. 570, 2021, p. 151015.

[22] Zhang, Y., Wu, Y., Jiang, Y., Wang, L., Zhang, J., Adsorbed film and synergistic effect of Benzyltriphenylphosphonium chloride and l-Histidine for magnesium alloys corrosion in NaCl, Journal of Alloys and Compounds, vol. 849, 2020, p. 156230.

[23] Jin, L., Jiuyi, L., Weishuang, Y., Yili, D., Biocorrosion characteristics of the copper alloys BFe30-1-1 and HSn70-1AB by SRB using Atomic Force Microscopy and Scanning Electron Microscopy, International Biodeterioration and Biodegradation, vol. 64, no 5, 2010, p. 363-370.

[24] Narenkumar, J., Elumalai, P., Subashchandrabose, S., Megharaj, M., Balagurunathan, R., Murugan, K., Aruliah, R., Role of 2-mercaptopyridine on control of microbial influenced corrosion of copper CW024A metal in cooling water system, Chemosphere, vol. 222, 2019, p. 611-618.

[25] Haitham, M.W., Mohsin, T.M., Tariq, K.A., Structure and characteristics of Nb₂O₅ nanocoating thin film for biomedical applications, Materials Today: Proceedings, 2022.

[26] Inime, I.U., Hongwei, S., Enobong, F.D., Jianyang, L., Songhua, G., Fuchun, L., En-Hou, H., Active anticorrosion and self-healing coatings: a review with focus on multi-action smart coating strategies, Journal of Materials Science and Technology, vol. 116, 2022, p. 224-237.

[27] Anisimova, N., Martynenko, N., Novruzov, K., Rybalchenko, O., Kiselevskiy, M., Rybalchenko, G., Straumal, B., Salishchev, G., Mansharipova, A., Kabiyeva, A., Gabdullin, M., Dobatkin, S., Estrin, Y., Modification of biocorrosion and cellular response of magnesium alloy WE43 by multiaxial deformation, Metals, 2022, vol. 12, no. 1, 2022, p. 105.

[28] Steiner Petrovič, D., Mandrino, D., Šarler, B., Horky, J., Ojdanic, A.J., Zehetbauer, M., Orlov, D., Surface analysis of biodegradable Mg-alloys after immersion in simulated body fluid, Materials, 2020, vol. 13, no. 7, 2020, p. 1740.

[29] Rivero, P.J., Redin, D.M., Rodríguez, R.J., Electrospinning, a powerful tool to improve the corrosion resistance of metallic surfaces using nanofibrous coatings, Metals, vol. 10, no. 3, 2020, p. 350.

[30] Qingyu, Q., Jin, X., Boxin, W., Qi, F., Changkun, Y., Cheng, S., Zhenyao, W., Biotic enhancement of *Desulfovibrio desulfuricans* on multi-factor influenced corrosion of X80 steel in saline soil, Corrosion Science, vol. 200, 2022, p. 110228.

[31] Bruna, C.E., Schibicheski, K., Gelson, B.S., Serbena, F.C., Lepienski, C.M., Chuproski, R.F., Borges, P.C., Improved saline corrosion and hydrogen embrittlement resistances of superaustenitic stainless steel by PIII nitriding, Journal of Materials Research and Technology, vol. 18, 2022, p. 1717-1731.

[32] Majd, M.T., Ramezanzadeh, M., Bahlakeh, G., Ramezanzadeh, B., Steel corrosion lowering in front of the saline solution by a nitrogen-rich source of green inhibitors: detailed surface, electrochemical and computational studies, Construction and Building Materials, vol. 254, 2020, p. 119266.

[33] Dehoux, A., Bouchelaghem, F., Berthaud, Y., Micromechanical and microstructural investigation of steel corrosion layers of variable age developed under impressed current method, atmospheric or saline conditions, Corrosion Science, vol. 97, 2015, p. 49-61.