



Inhibition Effect of Butan-1-Ol on the Pitting Corrosion of Austenitic Stainless Steel (Type 304)

Roland T. LOTO^{1, 2, *}

¹*Department of Mechanical Engineering, Covenant University, Ota, Ogun State, NIGERIA*

²*Department of Chemical, Metallurgical & Materials Engineering, Tshwane University of Technology, Pretoria, SOUTH AFRICA*

Received: 20/01/2015

Accepted: 15/02/2016

ABSTRACT

The performance of Butan-1-ol (BTU) on the pitting corrosion inhibition of austenitic stainless steel (Type 304) in dilute sulphuric acid contaminated with recrystallized sodium chloride was investigated with the aid of potentiodynamic polarization technique. Corrosion potential, pitting potential, passivation potential, nucleation resistance, passivation range, passivation capacity measurements and potentiodynamic analysis were used to assess the pitting resistance characteristics of the stainless steel. Results showed that pitting potential increased progressively with proportionate increase in BTU concentration. This occurred with corresponding increase in the passivation range which shows an enhanced resistance to pitting corrosion..

Key Words: *Corrosion, pitting, sulphuric acid, steel; inhibitor.*

1. INTRODUCTION

Austenitic stainless steel is one of the most versatile metals for applications in buildings as construction material and in various harsh conditions such as in chemical industries, desalination and waste water treatment plants, petroleum industry and metal extraction industries due to its resistance to general corrosion, high

temperature mechanical properties, good fabricability and weldability. The corrosion resistance property is basically due to the passive film formed instantaneously on the steels and has been intensively studied using different surface analysis techniques [1-4]. A chemical combination of iron and chromium oxides formed, with hydroxide and H₂O concentrated at the outermost region

of the film constitutes the passive film [5-7]. Exposure of austenitic stainless in corrosive aqueous solution causes chromium oxides to enrich at the metal/film interface resulting in the passive layer, which is responsible for its excellent corrosion properties [8-11]. In the presence of aggressive ions, such as chloride anion in seawater, mineral acids etc. local breakdown of passivity occurs, mainly at regions of local heterogeneities, inclusions and impurities causing pitting corrosion.

Pitting corrosion is a localized electrochemical dissolution process which in most cases causes catastrophic failure of passive metals. In this form of corrosion only small areas of the metal surface undergo localized attack, rapidly penetrating into the metal whilst the rest of the surface remains largely unaffected and probably passive [12, 13]. The pitting corrosion resistance of austenitic stainless steels depends on their chemical composition and metallurgical microstructure. Pits location on passive metals is often unpredictable being randomly dispersed on the metal surface especially at non-metallic inclusions [14-17]. Passivity breakdown is followed by pit nucleation, growth, and sometimes repassivation on highly resistant metals [18, 19]. When the rate of passivation is lower than the rate of film destruction, the film does not recover sufficiently and the microscopically formed pit continues to grow consequentially leading to an active macroscopic pit. The consequential process occurs in three steps: nucleation, metastable pit propagation and stable pit propagation [20-23].

A number of organic compounds have been used in the inhibition of general metallic corrosion [24-27]; however the application of organic inhibitors for pitting corrosion inhibition of stainless steels is limited. Pitting corrosion is a complicated localized corrosion phenomenon and the relationship between adsorption of organic compounds and corrosion inhibition applicable in general corrosion is not obvious. This research aims to investigate the inhibition effect of butan-1-ol, and organic compound on pitting corrosion of austenitic stainless steel (Type 304) in dilute sulphuric acid. Butan-1-ol (BTU) is a primary alcohol which occurs naturally as a minor product of the fermentation of sugars and other carbohydrates [28-33]. The largest use of butan-1-ol is as an industrial intermediate, particularly for the manufacture of butyl acetate.

2. EXPERIMENTAL METHODS

Material

Commercially available Type 304 austenitic stainless steel (ASS) was used for all experiments. Analysis from the Applied Microscopy and Triboelectrochemical Research Laboratory, Department of Chemical and Metallurgical Engineering, Tshwane University of Technology, South Africa with average nominal composition of 18.11% Cr, 8.32% Ni and 68.32% Fe. The material is cylindrical with a diameter of 18 mm.

Inhibitor

Butan-1-ol (BTU) a brownish, translucent liquid is the inhibitor used. The structural formula of BTU is shown in

Fig. 1. The molecular formula is C_4H_9OH while the molar mass is 74.122 g/mol.



Figure. 1 Chemical structure of Butan-1-ol (BTU)

BTU was applied in concentrations of 2.5%, 5%, 7.5%, 10%, 12.5% and 15% per 200ml of 3 M H_2SO_4 solutions respectively.

Test Media

3M H_2SO_4 acid with 3.5% recrystallized sodium chloride of analar grade was used as the corrosion test media.

Preparation of Test Specimens

The cylindrical stainless steel (18 mm dia.) was mechanically cut into a number of test specimens of dimensions in length ranging from 17.8 mm and 18.8 mm coupons. The two surface ends of each of the specimen were ground with silicon carbide abrasive papers of 80, 120, 220, 800 and 1000 grits. They were then polished with 6 μm to 1 μm diamond paste, washed with distilled water, rinsed with acetone, dried and stored in a desiccator for linear polarization test.

Linear Polarization Resistance

Linear polarization measurements were carried out using, a cylindrical coupon embedded in resin plastic mounts with exposed surface of 254 mm². The electrode was metallographically prepared with specific grades of silicon carbide paper, polished to 6 μm , rinsed by distilled water and dried with acetone. The studies were performed at ambient temperature of 25 °C with Autolab PGSTAT 30 ECO CHIMIE potentiostat and electrode cell containing 200 ml of electrolyte, with and without BTU inhibitor. A graphite rod was used as the auxiliary electrode and silver chloride electrode (Ag/AgCl) was used as the reference electrode. The steady state open circuit potential (OCP) was noted. The potentiodynamic studies were made from -1.5V versus OCP to +1.5 V versus OCP at a scan rate of 0.00166V/s and the corrosion currents were registered. The corrosion current density (I_{cr}) and corrosion potential (E_{cr}) were determined by the intersection of the extrapolated anodic and cathodic Tafel lines. The pitting potential E_{pit} , and passivation potential E_{pp} , were determined from the polarization curve.

3. RESULTS AND DISCUSSION

Nucleation resistance, passivation capacity, passivation range and passivation potential

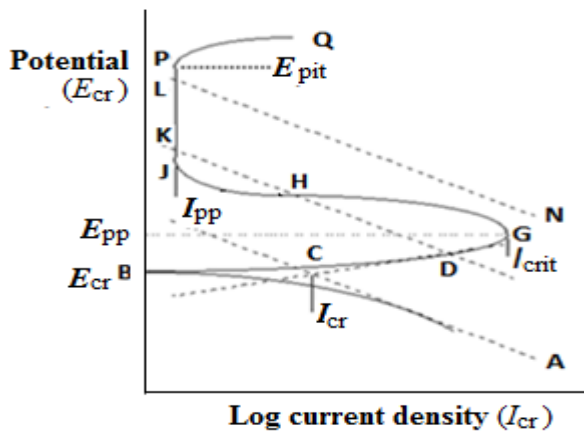
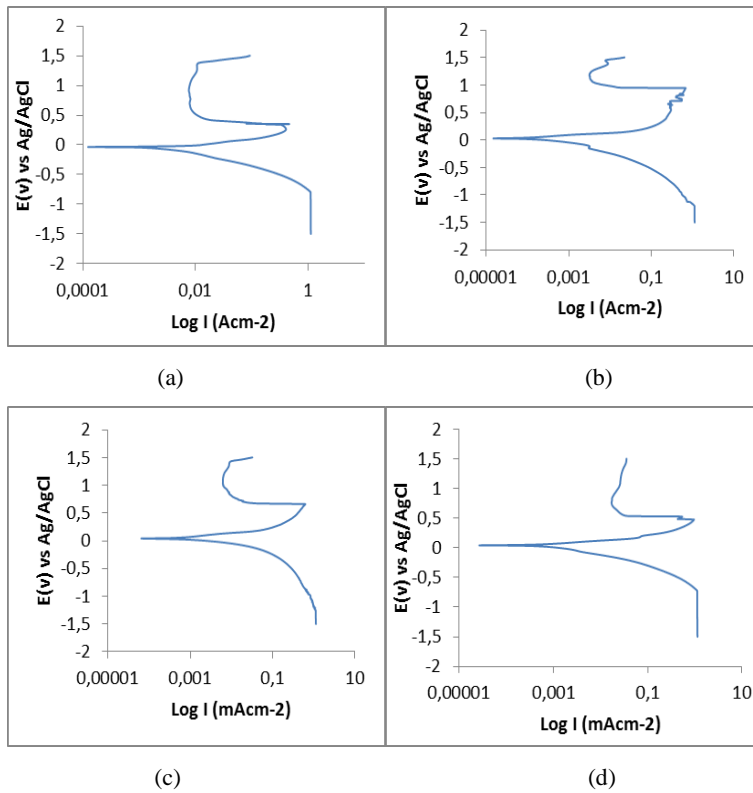


Figure 2. Schematic potentiodynamic polarization behaviour of passivating metals

Figure 2 is a representative polarization plot of the variation of corrosion potential (E_{cr}) with the log of current density (I_{cr}) for the stainless steel in dilute sulphuric acid /chloride media.

- AB represents cathodic reaction.
- BG represents anodic dissolution reaction. The metal is not passivated at the corrosion potential (E_{cr} , B).

- AC and DC are Tafel straight lines
- At potentials more positive than B, corrosion rate increases, and reaches a maximum at the passivation potential/ critical current I_{crit} at point G, which is given the symbol, E_{pp} .
- The transition from active dissolution occurs in the region G to J. A protective film begins to form and causes a sudden drop in corrosion current density.
- From J to P, the passive zone, the current density is maintained until point P.
- At P (pitting potential E_{pit}), breakdown of the protective film begins. It is here that the likelihood of pitting is greatest, and consequently specimen failure.
- E_{pit} often called the critical pitting or breakdown potential is a useful parameter in assessing pitting corrosion properties of materials.



(a)

(b)

(c)

(d)

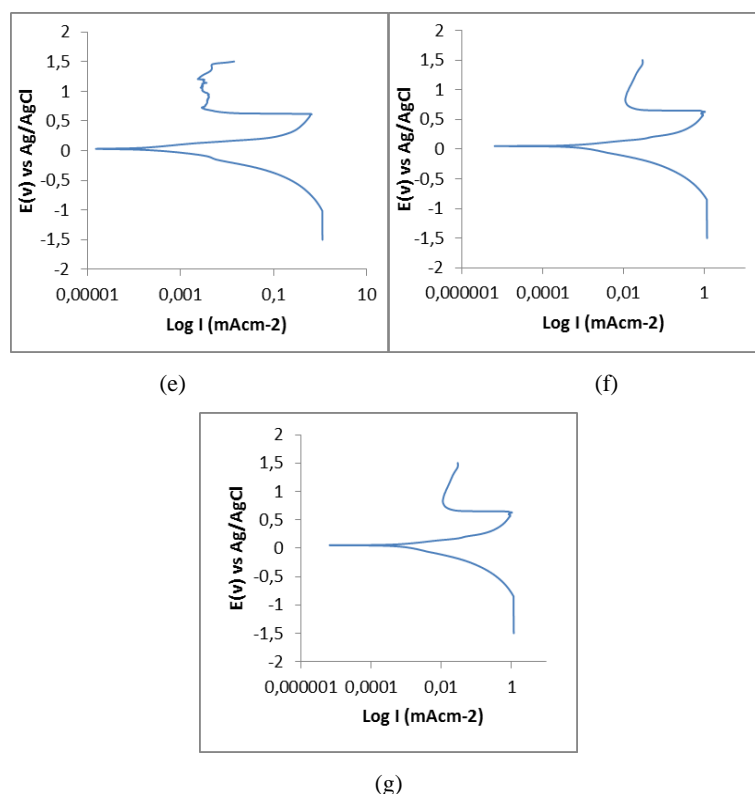


Figure. 3(a-g): Polarization scans for austenitic stainless steel in 3M H₂SO₄ solution at (0-15%) BTU concentration

Table 1. Potentiostatic values of austenitic stainless steel in 3M H₂SO₄/ BTU

Sample	BTU Concentration (%)	Pitting Potential, E_{pit} (V)	Passivation Potential (V)	Passivation Range (V)	Nucleation Resistance (V)	Passivation Capacity (V)	Corrosion Potential, E_{cr} 'Cal' (V)
A	0%	1.258	0.663	0.596	1.294	0.699	-0.036
B	2.5%	1.381	1.054	0.326	1.353	1.026	0.028
C	5%	1.395	0.804	0.591	1.358	0.766	0.037
D	7.5%	1.371	0.699	0.671	1.334	0.662	0.037
E	10%	1.367	0.695	0.672	1.334	0.662	0.033
F	12.5%	1.449	0.685	0.763	1.402	0.638	0.047
G	15%	1.449	0.679	0.770	1.402	0.632	0.047

The polarization scans for austenitic stainless steel in 3M H₂SO₄ solution at (0-15%) BTU concentrations are shown in Figure 3(a-g). The effects of BTU at the stated concentrations are significant on the potentiostatic parameters (E_{pit} , E_{cr} and E_{pp}) shown in Table 1 and hence the pitting resistance of the stainless steel. The pit nucleation resistance NR ($E_{pit} - E_{cr}$), passivation range ($E_{pit} - E_{rep}$) and repassivation capacity RC ($E_{rep} - E_{cr}$) can be considered to be a measure of the susceptibility of alloys to pitting corrosion [34-38]. Alloys exhibiting higher values of nucleation resistance and lower values of repassivation capacity are more resistant to pitting corrosion. The values of NR and RC are shown in Table 1. Nucleation occurrence is due of the creation and

evolution of metastable pits. This pits forms and develops for short period before repassivation at potentials well below the pitting potential and during the induction time before the onset of stable pitting at potentials above the pitting potential [39-40]. The nucleation phase of pitting corrosion entails the collapse of the protective passive film, presence of localised gradients responsible for pit propagation. The pitting corrosion mechanism has been the subject of serious debate for quite a while [41-46]. Transition from nucleating to pit propagating is subject to the fact that within chloride media, the solution within the pit hole becomes very corrosive and highly concentrated with chloride ions resulting in metal dissolution instead of the steel passivating. The chloride ions transport into

the active corrosion regions of the steel to counteract the excessive amounts of metallic ions. This causes increased acidity due to the highly concentrated chloride solution which has an average ionic activity coefficient higher than one. There are also concentration and potential gradients responsible for the migration of metal ions to the pit exterior. A pit will only initiate if the rate of metal dissolution is greater than the rate of passivation in order to sustain the pit acidity that will maintain the dissolution.

Influence of BTU on the Pitting Corrosion Evaluation of ASS in 3 M H₂SO₄

Severe active general corrosion reactions of anodic dissolution of ASS alloy occurred in the presence of the corrosive anions, (Cl⁻ and SO₄²⁻), in all BTU concentrations at high potentials due to pitting failure. Detailed observation of Fig. 3(b-d) shows that increase in BTU concentration has a limited influence on the polarization curve. Corrosion failure occurs almost instantaneously at the pitting potential as a result of the inability of BTU to sustain its protective film most probably due to the weak van der Waals forces responsible for its bonding to the steel surface. This is further confirmed from the low inhibition efficiencies results obtained until 12.5% - 15% BTU concentration where the inhibition efficiency is high.

At these concentrations (12.5% - 15%) transpassivity is totally absent, but its overall influence is negligible. The pitting potential values (E_{pit} , Table 1), increased with increasing BTU concentration from sample A to G, an indication of the ability of BTU to delay the formation of pits after 0% BTU concentration. Fig. 4 shows the plot of E_{pit} versus BTU concentration. The E_{pit} illustrate the inhibitive performance of BTU in pit formation. Pitting occurred at potentials slightly above the values obtained for 0% BTU. The passivation range showed a relative increase consistent with the increase in passivity of the steel as the concentration of BTU increases. The potential at which ASS repassivates reduces progressively with increase in BTU concentrations, with the exception of sample B where there was a sharp increase in the repassivation potential due to BTU desorption at this particular concentration. For the remaining samples the repassivating potential values shows the capacity of BTU to enhance the steels passivation characteristics against corrosion, but the overall impact on the general corrosion rate is negligible until 12.5% - 15% BTU concentration where the inhibition efficiency was significantly high. The decrease in RC coincides with increase in nucleation resistance.

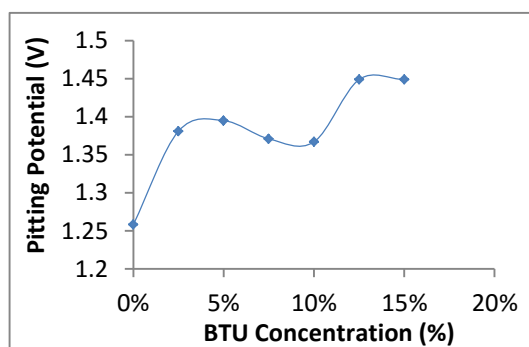


Figure.4 Plot of E_{pit} versus BTU Concentration

4. CONCLUSION

Potentiodynamic polarization tests, on austenitic stainless steel samples in dilute sulphuric acid contaminated with sodium chloride in the presence of butan-1-ol (BTU) inhibiting compound show that the pitting potential (E_{pit}), of the steel increased with increase in BTU concentration. The values obtained from nucleation resistance, passivation capacity and passivation range from the polarization plot at all concentrations of BTU studied showed the significant of BTU on the increased pitting corrosion resistance of austenitic stainless steel.

ACKNOWLEDGEMENTS

The authors acknowledge the Department of Chemical, Metallurgical and Materials Engineering, Faculty of Engineering and the Built Environment, Tshwane University of Technology, Pretoria, South Africa for the provision of research facilities for this work.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

REFERENCES

- [1] Jong, J.K., Yu, M.Y., "Study on the Passive Film of Type 316 Stainless Steel, *Int. J. of Elect. Sci*", 8: 11847-11859 (2013).
- [2] Wegelius, L., Falkenberg, F. and Olefjord, I., "Passivation of Stainless Steels in Hydrochloric Acid", *J. of Elect. Soc.*, 146: 1397-1406 (1999).
- [3] Bastidas, J.M., Lopez, M.F., Gutierrez, A. and Torres, C.L., "Chemical analysis of passive films on type AISI 304 stainless steel using soft X-ray absorption spectroscopy", *Corros. Sci.*, 40: 431-438 (1998).
- [4] Bastidas, J.M., Torres, C.L., Cano, E. and Polo, J.L., "Evaluation of the protective properties of natural and artificial patinas on copper. Part I. Patinas formed by immersion", *Corros. Sci.*, 44: 625-633 (2002).
- [5] Azam, M.A., Isomura, K., Fujiwara, A. and Shimoda, T., "Towards realization of high performance electrochemical device using vertically-aligned single-walled carbon nanotubes grown from ethanol", *Global Engineers & Technologists Rev.*, 1: 1-8 (2011).
- [6] Azam, M.A., Fujiwara, A. and Shimoda, T., "Thermally oxidized aluminum as catalyst-support layer for vertically aligned single-walled carbon nanotube growth using ethanol", *Appl. Surf. Sci.*, 258: 873-882 (2011).
- [7] Llewellyn, D.T. and Hudd, R.C., "Stainless steel", *Steels*, 291-379: (1998).

- [8] Marcus, P. and Olefjord, I., "A Round Robin on combined electrochemical and AES/ESCA characterization of the passive films on Fe-Cr and Fe-Cr-Mo alloys", *Corros. Sci.*, 28: 589-602 (1988).
- [9] Pardo, A., Merino, M.C., Coy, A.E., Viejo, F., Arrabal, R. and Matykina, E. "Effect of Mo and Mn additions on the corrosion behaviour of AISI 304 and 316 stainless steels in H₂SO₄", *Corros. Sci.*, 50: 780-794 (2008).
- [10] Pardo, A., Merino, M.C., Coy, A.E., Viejo, F., Arrabal, R. and Matykina, E., "Pitting corrosion behaviour of austenitic stainless steels – combining effects of Mn and Mo additions", *Corros. Sci.*, 50: 1796-1806 (2008).
- [11] Jegdic, B., Drazic, D.M. and Popic, J. P., "Open circuit potentials of metallic chromium and austenitic 304 stainless steel in aqueous sulphuric acid solution and the influence of chloride ions on them", *Corros. Sci.*, 50: 1235-1244 (2008).
- [12] Turnbull, A., McCartney, L.N. and Zhou, S., "A model to predict the evolution of pitting corrosion and the pit-to-crack transition incorporating statistically distributed input parameters", *Corros. Sci.*, 48: 2084-2105 (2006).
- [13] Kondo, Y., "Prediction of Fatigue Crack Initiation Life Based on Pit Growth", *Corrosion J.*, 45: 7-11 (1989).
- [14] Isaacs, H.S., "The localized breakdown and repair of passive surfaces during pitting", *Corros. Sci.*, 29: 313-23 (1989).
- [15] Macdonald, D.D., "The Point Defect Model for the Passive State", *J. of Elect. Soc.*, 139(12): 3434-3449 (1992).
- [16] Burstein, G.T., Liu, C., Souto, R. M. and Vines, S. P., "Origins of pitting corrosion. Corrosion Engineering", *Science and Tech.*, 39(1): 25-30 (2004).
- [17] Djoudjou, R., Lemaitre, C. and Beranger, G., "Role of sulphide inclusions on the pitting of stainless steels in chloride media", *Corrosion Reviews*, XI(3/4): 157-176 (1993).
- [18] Burstein, G.T., Pistorius, P. C., Mattin, S. P., "The nucleation and growth of corrosion pits on stainless steel", *Corros. Sci.*, 35(1-4): 57-62 (1993).
- [19] Pistorius, P.C., Burstein, G. T., "Detailed Investigation of Current Transients from Metastable Pitting Events on Stainless Steel - The Transition to Stability", *Mats. Sci. Forum*, 111-112: 429-452 (1992).
- [20] Isaacs, H.S., Newman, R.C., Chemistry within Pits, Crevices and Cracks edited by A. Turnbull, London, 45 (1987).
- [21] Isaacs, H.S., "The localized breakdown and repair of passive surfaces during pitting", *Corros. Sci.*, 29: 313-323 (1989).
- [22] Pistorius, P.C. and Burstein, G. T., "Detailed Investigation of Current Transients from Metastable Pitting Events on Stainless Steel", *Phil. Trans. of the Royal Soc.*, 341:531-559 (1992).
- [23] G. T. Burstein, S. P. Mattin: Philosophical Magazine Letters, 66, 127-131, (1997).
- [24] Srhiri, A., Etman, M., Dabosi, F., "Electro and physicochemical study of corrosion inhibition of carbon steel in 3% NaCl by alkylimidazoles", *Electrochimica Acta*, 41: 429-437 (1996).
- [25] Ita, B.I. and Offiong, O.E., "Organic sulphur-containing compounds as corrosion inhibitors for mild steel in acidic media: correlation between inhibition efficiency and chemical structure", *Materials Chemistry and Physics*, 48: 164 -169 (1997).
- [26] Bouayed, M., Raba, H., Srhiri, A., Saillard, J.Y., Bachir, A.B. and Beuze, A.L., "Experimental and theoretical study of organic corrosion inhibitors on iron in acidic medium", *Corros. Sci.*, 41: 501-517 (1998).
- [27] Fonsati, M., Zucchi, F. and Trabaneli, G., "Study of corrosion inhibition of copper in 0.1 M NaCl using the EQCM technique", *Electrochimica Acta*, 44: 311-322 (1998).
- [28] Hazelwood, L.A., Daran, J., Van Maris, A. J. A., Pronk, J. T., Dickinson, J. R. and Richard, J., "The Ehrlich pathway for fusel alcohol production: a century of research on *Saccharomyces cerevisiae* metabolism", *Appl. & Environ. Microb.*, 74(8): 2259-2266 (2008).
- [29] Mellan, I., Industrial Solvents, 482 (1950).
- [30] Doolittle, A.K., The Technology of Solvents and Plasticizers, 644 (1954).
- [31] Butanols, four isomers, Environmental Health Criteria monograph, 65 (1987).
- [32] Monich, J.A., Alcohols, Their Chemistry, Properties and Manufacture, New York, Chapman and Reinhold, (1968).
- [33] Amundsen, J., Goodwin, R. J., Wetzel, W. H., Water-soluble Pentachlorophenol and Tetrachlorophenol Wood-Treating Systems, (1979).
- [34] Ajit, K.M. and R. Balasubramaniam, R., "Corrosion inhibition of aluminium by rare earth chlorides", *Mats. Chem. & Phys.*, 103(2-3): 385-393 (2007).
- [35] Aramaki, K., "The inhibition effects of cation inhibitors on corrosion of zinc in aerated 0.5 M NaCl", *Corros. Sci.*, 43: 1573-1588 (2001).

- [36] Bethencourt, M., Botana, F. J., Calvino, J. J., Marcos, M. and Rodríguez-chacón, M. A., *Corro. Sci.*, 40(11): 1803-1819 (1998).
- [37] Bethencourt, M., Botana, F. J., Cauqui, M. A., Marcos, M., Rodríguez, M.A. and Rodríguez-izquierdo, J. M., "Protection against corrosion in marine environments of AA5083 Al-Mg alloy by lanthanide chlorides", *J. of Alloys and Compds.*, 250(1-2): 455 - 460 (1997).
- [38] Lihua, Z., Wei, Z., Yiming, J., Bo, D., Daoming, S., Jin, L., "Influence of annealing treatment on the corrosion resistance of lean duplex stainless steel 2101", *Electrochimica Acta*, 54(23): 5387-5392 (2009).
- [39] Popov, Yu.A., "Theory of pit nucleation. II. Interaction between pits at the early stage of development. The role of solvent", *Prot. of Mets.*, 44(2): 126-133 (2008).
- [40] Strehblow, H.H., "Nucleation and Repassivation of Corrosion Pits for Pitting on Iron and Nickel", *Mats. & Corr.*, 27(11):792-799 (1976).
- [41] Suter, T., H. Boehni, H., "A new microelectrochemical method to study pit initiation on stainless steels", *Electrochim. Acta*, 42: 3275-3280 (1997).
- [42] Riley, A. M., Wells, D. B., Williams, D. E., "Initiation events for pitting corrosion of stainless steel", *Corros. Sci.*, 32: 1307-1313 (1991).
- [43] Williams, D. E., Newman, R. C., Song, Q., Kelly, R. G., "Passivity breakdown and pitting corrosion of binary alloys", *Nature*, 350: 216-219 (1991)
- [44] Burstein, G. T., Mattain, S. P., "in Critical Factors in Localized Corrosion II", P.M. Natishan, R. G Kelly, G. S. Frankel, and R. C. Newman, Editors, PBV 95-15, The Electrochem. Soci. Pro. Series, Pennington NJ, USA, 1996, p.1
- [45] Lin, L.F., Chao, C. Y., Macdonald, D. D., A point defect model for anodic passive films II. Chemical breakdown and pit initiation. *J. Electrochem. Soc.*, 128: 1194-1198 (1982).
- [46] Kobayashi, Y., Virtanen, S., Bohni, H., Microelectrochemical studies on the influence of Cr and Mo on nucleation events of pitting corrosion *J. Electrochem. Soc.*, 147(1): 155-159 (2000)