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Short Communication

Investigation of Corrosion of A and E36 Naval Steels Using Potentiodynamic Polarization and Modified Prohesion Test

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Our research paper aims to investigate the effects of 0.4% ammonium sulphate and 0.05% sodium chloride mixture solution (Prohesion test) on the corrosion behavior of A and E36 naval steels tested at the room temperature. The corrosion investigations have been investigated using electrochemical method such as potentiodynamic polarization curves and gravimetric method. Subsequently, the samples were subjected to morphological and compositional analyzes by scanning electron microscopy. The corrosion behavior of the A and E36 naval steels were determined from breakdown potential using potentiodynamic polarization method. The results of the electrochemical tests and gravimetric method indicate that the E36 naval steel sample has better corrosion resistance than A naval steel sample.

Keywords: Corrosion resistance; Naval steels; Potentiodynamic polarization; Electrochemical method

1. INTRODUCTION

The naval steel is a thick, hot-rolled, high corrosion and abrasion resistant sheet used in the shipbuilding industry for shipbuilding and various component parts. In recent years, greater importance has been given to the safety, sustainability and protection of ships to corrosion of the marine environment. The corrosion process occurs as reduction or oxidation reactions, the metal goes to anode site and transfers the electrons to the cathode site. The corrosion products are formed because the ions reacts with the substances from the environment, and these products adhere to the surface of the metal [1]. For metals, the metallic state is thermodynamically unstable in the presence of chemical agents from marine water and not only, having the tendency to corrode and to recreate the initial form from which they comes from.

The corrosion includes all chemical and electrochemical processes that result in spontaneous and continuous degradation of metal and alloy surfaces [1].

Studying the corrosion behavior of low alloy steel in 10% NaCl, Hui bin We found that the pitting corrosion for E36 grade naval steel was inclined to occur around the place where the inclusion exists [2].

Andi Rustandi found that the austenitic stainless steel type 304L and 316L, have the lowest corrosion resistance at 3.5 w/v NaCl, due to dissolved oxygen solubility that reaches its maximum point [1].

The protection of materials in the shipbuilding industry is a process in which the ships must be protected by the corrosion effect of the environments factors. The methods of protection are based on corrosion processes theory. The factors that affect the slowing down or stopping of the corrosion process can be determined by the alteration of the material properties and environment [3].

One of the corrosion damage under tension occurs when the process is localized and it progresses through alternative stages of pitting corrosion and cracks propagation. These cracks are the result of the brittle fractures occurring at much lower tensions than those offered by the resistance characteristics of the material [4-8].

Using polarization techniques by studying material polarization treatment, it is considered a suitable way for the investigation of naval steel corrosion. For this analysis, it is used potentiodynamic polarization (PD), which is a good way to investigate the start of passivity, and the breakdown of oxide layers. It can be calculated also the rate of pitting corrosion because of the large range of scanning potential. The purpose of this study is to use the PD method to predict and explain the behavior of materials corrosion.

The use of polarization methods offers the best alternative for corrosion tests of different naval steel used for boat fabrication. As Gheorghies et all. [8] showed in their paper the degradation process of naval steel is a localized corrosion process called pitting; These areas are zones from where the fatigue cracks are initiated and propagated.

This method of electrochemical polarization allows the reaction rate to be determined at the electrode interface or at the solution surface during the experimental recordings to determine the corrosion rate [7, 9-10].

As Runzhi Qin et all. present in their work the corrosion kinetics of reaction that take place can be explained using the results from polarization curves. In this study they found that the presence of SO_4^{2-} ions from the soil eases the dissolution of steel in solution depending on different concentration of SO_4^{2-}ions. Also, there are presented in the literature, theories on the dissolution of steel that have been reported by Runzhi Qin et all. [11, 12], and it was presented that the corrosion can be associated with the formation of Fe^{2+} ions [10, 13] event there other studies that consider the SO_4^{2-} ions can facilitate the dissolution of steel.

The objective of this paper is to evaluate the corrosion behavior of A and E36 naval steel samples in a mixture solution based on ammonium sulphate and sodium chloride. Corrosion properties have been studied using electrochemical method, such as potentiodynamic polarization curves and gravimetric method.

2. EXPERIMENTAL METHODS

For experimental research part, we used two type of naval steels used primarily in structural applications in marine / shipping industry for barges, ships, small vessels, support structures and various type of equipment, A36 (noted in this paper with A) and E36 purchased from Damen Shipyards (Galati, Romania). The chemical composition of naval steels A and E36 type is presented in Table 1.

Table 1. The chemical composition of naval steels type A and E36 samples.

Steel group	C max.	Mn	SI	P	S	Cu max.	Cr max.	Ni	Mo max.	Al
A	0.23	min. 25% C	max. 0.35	0.05	0.05	—				—
E36	0.18	0.90 — 1.60	0.10 — 0.50	0.04	0.04	0.35	0.2	0.20 — 0.40	0.08	min. 0.020

In Table 2. is presented the mechanical characterisation for A and E36 naval steel samples.

Table 2. The standard mechanical characteristics of normal and high strength steels used in shipbuilding for A and E36 naval steel.

Type of naval steels	Delivery state	Tensile strength (N/mm^2)	Yeld strength ReH (N/mm^2)	Elongation at break (%)	Test Temperature (°C)	Breaking load energy (KV,J)
A	Laminated	400…900	235	22	-	-
E36	Normalised	400…620	355	21	-40	34

The samples were mechanically cutted into square pieces of original parallelepiped-shaped sheet with the dimensions of 2 x 2 cm and 0.5 cm thickness as can be seen in Fig.1.

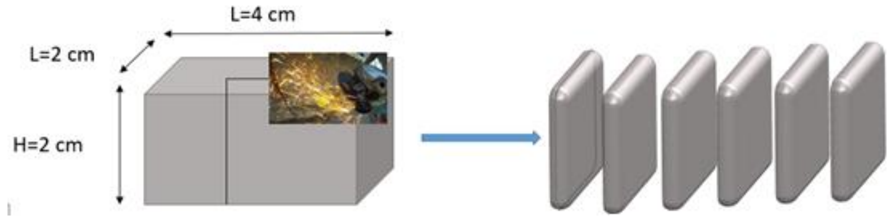


Figure 1. The schematic representation of cutted samples prepared for corrosion investigations

For the electrochemical measurements the steel samples were isolated on both surfaces with epoxy resin (CAF4, purchased from Bentley Addvanced Materials, UK), leaving only a well determined surface free for the study of corrosion 2.25 cm^2 . Before corrosion experiment, all samples were mechanically polished with sand paper and then were cleaned with hydrochloric acid, sodium hydroxide, washed with distilled water and finally dried. Electrochemical studies were achieved using a Voltalab

PGP 201 Radiometer analytical equipment. The experimental method for determination of anodic and cathodic polarization curves and the calculation of the corrosion parameters obtained by the extraction of the Tafel slopes were done with VoltaMaster program and Origin 8 to process the data obtained. All the experiments took place at 22^{0}C. The electrochemical cell measurement system contains three electrodes: the steel A or E36 samples served as working electrodes (WE), for counter electrode (CE) was used - platinum plate and the reference electrode (RE) used was Ag/AgCl (3M KCl) with a potential of +208 mV vs. NHE (normal hydrogen electrode). The schematic drown of electrochemical cell setup is presented in Fig. 2. The electrolyte used for experiments it was 150 mL and each test was triplicate in order to check the repeatability of the experiments.

To investigate the electrochemical corrosion of samples used for this study was applied potentiodynamic polarization method with scanning potential between -1.7 V to 0.99 V vs. Ag/AgCl (3M KCl) and a scan rate of 1mV/s.

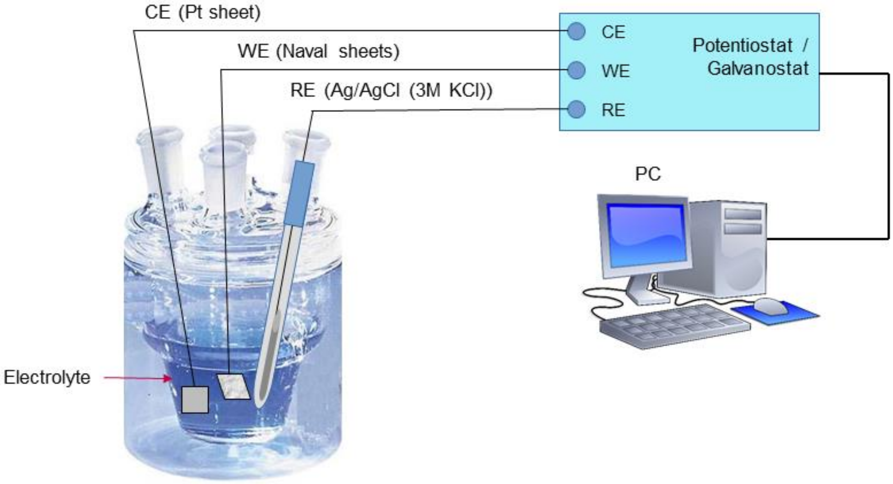


Figure 2. Schematic drown of electrochemical cell setup used for corrosion investigations of naval steels immersed in salt mixture 0.4% ammonium sulphate and 0.05% sodium chloride

The corrosion of A and E36 steel was also examined by gravimetric method at different times (0d (measurement 0 - before immersion, 1d (measurement 1 - 1day, 2d (measurement 2 - 2days...7d (measurement 7 - 7days from immersion time). The test performed at room temperature. To determine the weight loss corrosion of the naval steels (A and E36) all samples were weighed accurately before and after corrosion test every day using the analytical balance (Kern ALJ 500-4A, precision ± 0.1 mg). Before each weighing, the samples were dried. The test solution, for weight loss contain 40 mL the mixture of 0.4% ammonium sulphate and 0.05% sodium chloride (reagents that are used for Prohesion test). The pH of electrolyte used for corrosion investigations was measured using pH-metter (Toledo S20k) and have pH 5.2 ppt.

Prohesion test - ASTM G85 annex A5 - dilute electrolyte cyclic fog/dry test is also called "protection is adhesion" and it is used as an accelerated corrosion testing. This test shows the reality to which metal samples are subjected as blistering and delamination that are correlated with external agents [14-15].

The reagents used for this study were p.a purchased from Sigma Aldrich, NaCl ≥99% and $(NH_4)_2SO_4$ ≥99%. Chemical cleaning of the samples for gravimetric method is done in acid bath that cause the layer of formed oxide to split off on the surface of the metal. For steel materials, the solution is prepared using hydrocloric acid in concentration on 8 to 20% (Fig. 3a is the sample after the cutting and Fig. 3b is after chemical cleaning, and Fig. 3c is the samples immersed in salt mixture). After removing from the pickling bath the pieces were washed with water under pressure and then nutralized in calcinated soda bath with a concentration of 3 to 5%.

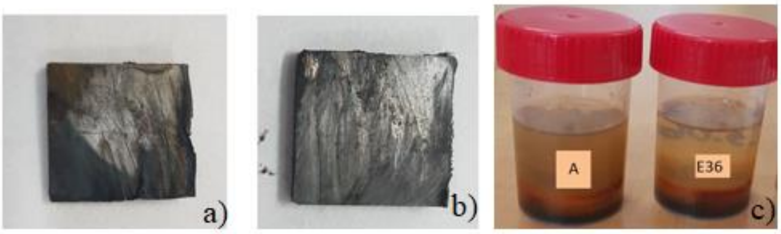


Figure 3. The steel surface sample after the cutting process (a), after the cleaning process, prepared for imersion in salt mixture (b) and the steel samples immersed in salt mixture 0.4% ammonium sulphate and 0.05% sodium chloride for 7 days to determine the weight loss by gravimetric method (c)

The metallographic microscope used was OLYMPUS UTV1X-2 in order to observe the variation of samples before corrosion test.

The FEI QUANTA 200 Scanning Electron Microscope was used to observe the morphological variations of the corrosion samples. The samples were also analyzed for chemical composition by energy dispersive X-ray spectroscopy (EDX) using software EDAX Genesis.

3. RESULTS AND DISCUSSION

3.1. Micrograph and Scanning Electron Microscopy of A and E36 naval steels

The steel sample surfaces for A and E36, before corrosion test through gravimetric and potentiodynamic polarization method, were evaluated using an optical metallographic microscope and are shown in Fig. 4. The micrograph image of the surface exposed (Fig. 4a for A grade steel) shows the ferrite (white areas)-perlite (grey-black areas) structure surface (Fig. 4b for E36 grade steel).

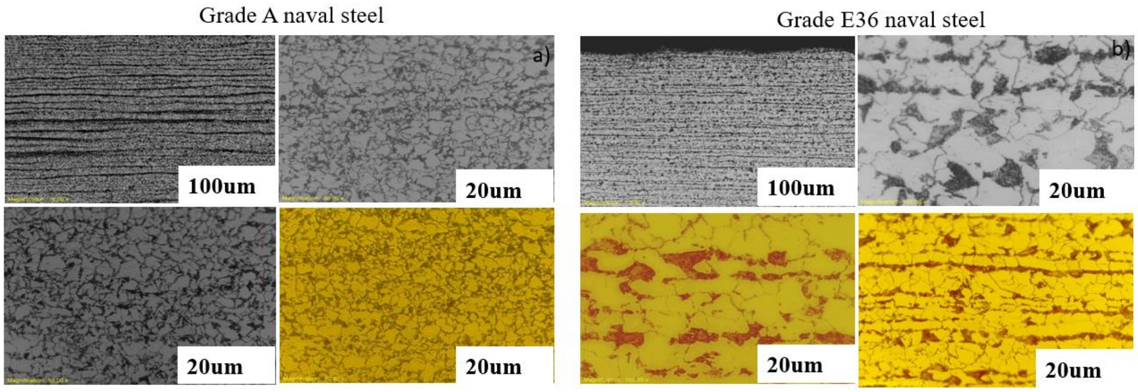
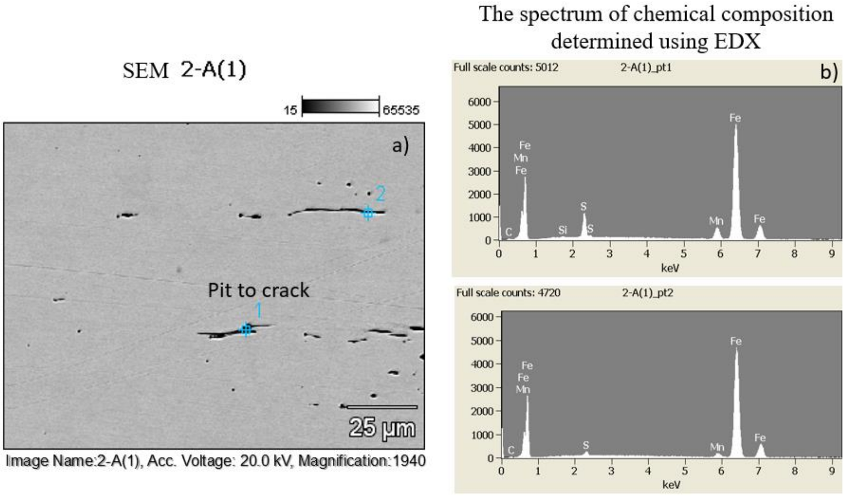


Figure 4. Micrograph images of steel surfaces before immersion test for (a) A steel grade and (b) E36

Figure 5 shows the SEM image of the surface of A (Fig. 5a) grade naval steel together with the elemental composition obtained from EDX analysis on selected area (Fig. 5b). In the superficial layer, of the samples is observed that the degradation takes place probably by increasing the depth of the pitting, pits that are localized in the ferrite phase and not due to the increase of their density.

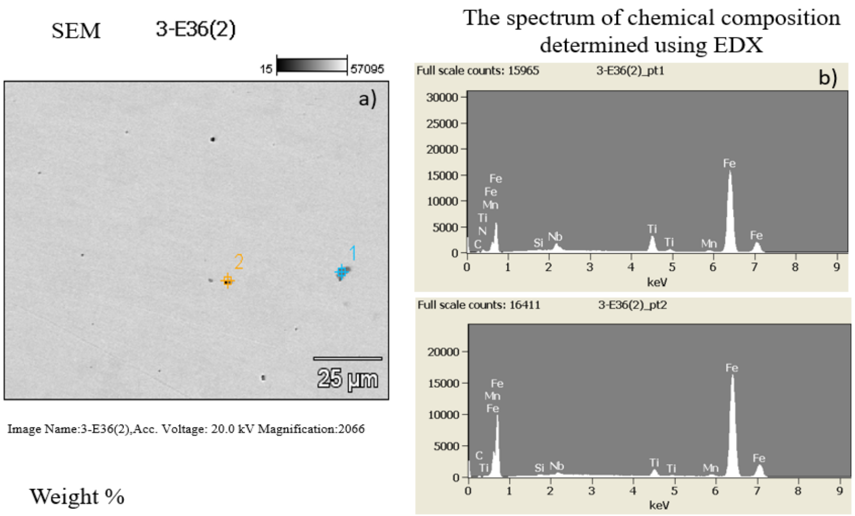


Weight %

	C-K	Si-K	S-K	Mn-K	Fe-K
2-A(1)_pt1	0.60	0.27	4.71	7.87	86.55
2-A(1)_pt2	0.61		0.89	3.40	95.10

Figure 5. The SEM images (a) and (b) EDX spectrum for A grade naval steel after immersion in salt mixture 0.4% ammonium sulphate and 0.05% sodium chloride

Figure 6 presents the SEM (6a) and EDX (6b) spectra for E36 grade naval steel. The steel studied has a ferrite-pearlite structure with homogeneous pearlite phase (solid solution) and heterogeneous phase as a ferrite Fe and cementite Fe, C [8]. Ferrite areas are less affected by the corrosive environment. In this way the surface layer features discontinuities and the first signs of pits can be observed after corrosion process. We can notice a smooth surface without many cracks. The mapping of elemental composition by EDX in the selected area is displayed also.



Weight %

	C-K	N-K	Si-K	Ti-K	Nb-L	Mn-K	Fe-K
3-E36(2)_pt1	1.06	2.01	0.29	7.75	4.42	1.55	82.91
3-E36(2)_pt2	1.02		0.30	2.87	1.47	1.84	92.50

Figure 6. The SEM images (a) and (b) EDX spectrum for E36 grade naval steel after immersion in salt mixture 0.4% ammonium sulphate and 0.05% sodium chloride

3.2. Potentiodynamic polarization and gravimetric method results used to determine the corrosion of tested samples

The corrosion behavior of A and E36 grade naval steel, has been studied by polarization measurements. The recorded Tafel plots are shown in Figure 7.

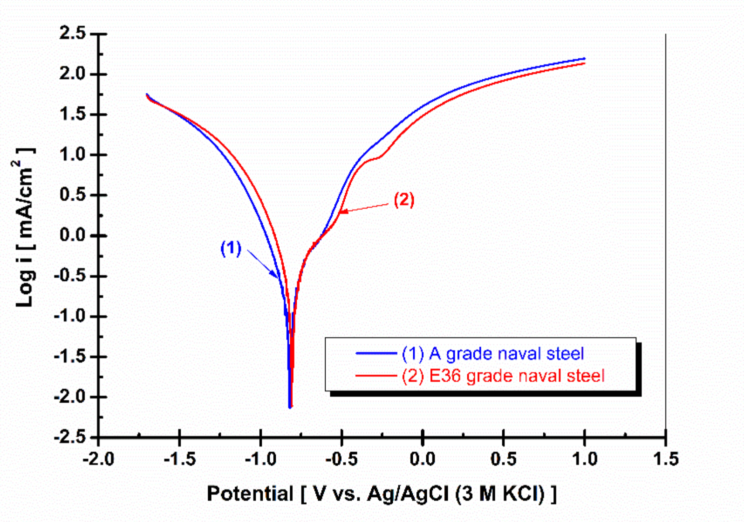


Figure 7. Potentiodynamic polarization curves of Tafel curves log |i| vs. potential for A and E36 naval steels samples immersed in salt mixture 0.4% ammonium sulphate and 0.05% sodium chloride at a scan rate of 1mV/s

From Figure 7 it can be seen that the corrosion current density has a smaller value attained for

E36 immersed in 0.4% ammonium sulphate and 0.05% sodium chloride mixture solution (0.3487 mA/cm^2) in comparison with A naval steel sample (0.5524 mA/cm^2), a smaller current density value means a higher polarization resistance and finally a lowest corrosion rate as penetration rate. The corrosion rate was calculated using Stern–Geary equation and the values are summarized in Table 3.

Table 3. Calculation of corrosion rate using Tafel method according to the Stern–Geary equation

Naval steels type	**i_{cor} (mA/cm^2)**	**E (mV)**	**CR (mm/Y)**
A	0.5524	-805	2.098
E36	0.3053	-837	1.159

The corrosion current densities were calculated by extrapolation of linear parts of anodic and cathodic curves to the point of intersection of the corresponding corrosion potential as is presented in literature [9, 10, 16-18]. The redox reaction that takes place on the surface of naval steel are represented in the following equation [17]:

Anodic reaction: $Fe \rightarrow Fe^{2+} + 2e^-$

Cathodic reaction: $1/2O_2 + H_2O + 2e^- \rightarrow 2\,HO^-$

These evolutions presented by Tafel curves allow for estimating the dependence of the corrosion current density of time, namely $i_{corr} = f(t)$, and inserted through Tafel curves. The increase in the mechanical stresses leads to an increase of the electrochemical processes, furthermore, leads to the apparition of localized corrosion on the surfaces tensioned [18].

Based on the analysis reported in the literature the first step of the corrosion is due to te Fe^{2+} ions that participate in the formation of rust. This type of rust looks like β-FeOOH than α-FeOOH [18]. The redox reaction that take place in the dissolution stage is: $4Fe^{2+} + 4H_2O + 2O_2 = 4FeOOH + 8H^+$

When the rust appears on the naval sheet in the presence of potentiostatic polarization there can be considered also transpassivation reaction in which the positive ion of iron changes electrons and transform in trivalent ion of Fe^{3+} as in the reaction: $2Fe^{2+} + 3H_2O = Fe_2O_3 + 6H^+ + 2e^-$.

In addition to the electrochemical studies (potentiodynamic polarization curves) presented above, gravimetric corrosion tests were performed. To determine the weight loss corrosion of the naval steels (A and E36) all samples were immersed in mixture solution (0.4% ammonium sulphate and 0.05% sodium chloride) and monitored 7 days. Every day at the same hour, the samples were weighed accurately after corrosion test using the analytical balance. The results of weighing the samples are summarized in Table 4, where: 0d is measurement 0 – before corrosion, in g; 1d is measurement 1 – after corrosion (first Day), in g; 2d is measurement 2 – after corrosion (2 Days from immersion), in g ..... 7d is measurement 7 – after corrosion (7 Days from immersion), in g.

Table 4. The results of weighing the samples A and E36 grade naval steels before and after corrosion during 7 days from immersion time

Steel type	0d	1d	2d	3d	4d	5d	6d	7d
A	4.3570g	4.3565g	4.3564g	4.3560g	4.3557g	4.3551g	4.3540g	4.3543g
E36	5.8251g	5.8251g	5.8249g	5.8248g	5.8247g	5.8246g	5.8244g	5.8242g

After that, the calculation of weight loss for a year by gravimetric method (results presented in Table 5) was done using the quality standards regarding the corrosion resistance or corrosion rate steels, following equation (1) [15]:

$$Ws = 10 \cdot \frac{Wc}{S \cdot D} \quad (1)$$

Where, Ws is the weight loss of the samples for a year, Wc is the weight loss after 7 days in mixture solution, S - the surface suposed to the corrosion and D is the density of the steel.

Table 5. The weight loss of the A and E36 grade naval steels during 7 days from immersion time

Steel Type	Wc (g)	S (m^2)	D (kg/dm^3)	Ws (µm/Y)
A	0.0027	$4x10^{-4}$	7.85	8.598
E36	0.0009	$4x10^{-4}$	7.85	2.66

The corrosion rate (CR) for the sample was calculated following equation (2) [16]:

$$\mathrm{CR} = \frac{\mathrm{Wi} - \mathrm{Wf}}{\mathrm{A} \cdot \mathrm{t}} \quad (2)$$

where: CR - corrosion rate, g/m^2h; Wi - initial weight of mild steel coupon, g; Wf - final weight of mild steel coupon, g; A - area of the coupon exposed at corrosion test, m^2; t the time of exposure (h).

After 7 days the corrosion rate for naval steel (grade A) determined by gravimetric method have a value by 0.04 g/m^2h while naval steel grade E36 have 0.013 g/m^2h.

4. CONCLUSIONS

In this research paper, we studied the corrosion behavior of two types of naval steel by electrochemical method and gravimetric method: A and E36 grade immersed in 0.4% ammonium sulphate and 0.05% sodium chloride mixture solution.

From our study can be conclude that the dissolution process started by localized corrosion process also called pitting. By optical microscopy and scanning electron microscopy, it can be observed areas on the surface of the samples where the fatigue cracks are initiated and propagated. It is also observed that E36 grade naval steel has a low value of corrosion rate (1.159 mm/Y) from the Tafel measurement than A grade naval steel which is 2.098 mm/Y, respectively.

Also, this result is demonstrated by the determination of CR using gravimetric method, for E36 having a lower value 0.013 g/m^2h than 0.04 g/m^2h for A grade naval steel. The corrosion rate of E36 steel is significantly decreased than A grade steel.

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CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Buruiana Daniela Laura, Herbei Elena Emanuela, Ceoromila Alina Mihaela, Busila Mariana: Conceptualization, Methodology, Writing- Reviewing and Editing. Trus Constantin, Bogatu Nicoleta (Simionescu), Ghisman Viorica: Investigation, Writing- Original draft preparation, Software, Validation.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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