EXPERIMENTAL STUDY OF MARITIME SHIPS CORROSION IN THE BLACK SEA, BY USING MAG-M MECHANIZED BUTT WELDING WITH METAL-CORED WIRE AND RUTILE FLUX-CORED WIRE

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Abstract. In this paper we analyze the corrosion behavior of the MAG-M mechanized butt welding with metal-cored wire and rutile flux-cored wire at two welding positions PA and PC at *in situ* conditions of the Black Sea. The following materials were used in this experimental programme: base material (high strength steel sheet EH 36, dimensions 300 x 150 x 10 mm), filler material (metal cored wire (E70C6MH4) and rutile flux-cored wire (E71T1MH4) according to AWS A5.18, diameter 1.2 mm) and auxiliary materials (M21- Corgon 18 gas mixture and flat concave channel ceramic support). The samples were immersed in sea water harvested in the Black Sea and then subjected to corrosion tests by electrochemical methods.

Key words: MAG-M welding, metal-cored wire, rutile flux-cored wire, marine corrosion

1. INTRODUCTION

Offshore vessels and structures spend almost 95% of their lifetime on the seaside once they are built. Therefore, the reduction in thickness due to the corrosion of the structure each element might lead to a decrease in global structure strength.

The steel is one of the most used materials in the shipbuilding industry and offshore structure (Kim *et al.*, 2012). Steel raises a major problem, because it shows a low corrosion resistance.

The marine environment is considered to be a very aggressive environment for almost all metallic materials, including the steel, known to be one of the most common materials for shipbuilding. Corrosion is a major cause of structural damage of marine and offshore structures. The corrosion of carbon steel in the marine environment becomes grave due to the very corrosive nature of the salty water and associated microorganisms (Mardare & Benea, 2017).

Many marine engineering structures are aging and deteriorating due to loss of material properties, exposure to severe environments, such as marine environments and/or increased workloads. Strengthening structurally damaged elements has traditionally been done by replacing elements by adding supports or by welding steel plates (Nguyen *et al.*, 2012). Metal structures are vulnerable to the corrosion of the marine atmosphere, especially in a polluted atmosphere due to chlorine concentration, acidification of thin films of electrolyte, wetting/drying effect and sufficient oxygen diffusion (Maa *et al.*, 2015).

Vessels are exposed to a number of corrosion environments and, as a result, corrosion patterns vary greatly depending on marine environment features in which they operate (Gudze & Melchers, 2008). Corrosion affects the effective loading capacity of the steel plates, causing the thinning of the steel plates. General or “uniform” corrosion, estimated as a result of experiments, is of primary interest. This kind of decay may involve the coalescence of several corrosion tanks of light or alloyed unprotected steels used in the construction of most vessels (Gudze & Melchers, 2008).

With regard to the operating life and mileage, ships are exposed to a wide range of different environmental factors that affect the rate of corrosion by loss of material and the formation of its various physical forms. Complex external factors, such as navigation in different areas with specific environments and on different routes, as well as atmospheric and seawater conditions, along with internal factors (arrangement of ballast tanks, dry spaces and cargo loads, operating conditions, etc.) cause a corrosion trend on ships in service (Ivosevič *et al.*, 2018).

The unique hydrological and hydrodynamics characteristics of the Black Sea confer the status of the largest anoxic basin in the world. The Black Sea is subject to environmental variations due to natural influences (i.e., climate change, global warming, sea level rise and coastal erosion). It is known that the corrosion of steels in fresh and salty waters is not only a function of salinity, but rather the balance of calcium-calcium carbonate (contents of water) and the acidity of the sea water, which is often high and show consistent fluctuations. Many structures and floating installations such as ships and offshore installations interacts with various forces due to the complexity of the this aggressive marine environment (Mardare & Benea, 2017).

These offshore structures are subjected predominantly to horizontal or vertical bending, although the side shell structures also experience local bending and stiffeners due to the wave action. The simple nature of the assessed structures provides insights that may be otherwise skewed by local stress concentrations in structures more prone to fatigue damage induced by corrosion appearance (Thompson, 2018).

This paper presents the results obtained for the corrosion of vessels in the specific conditions of the Black Sea marine environment, which is different from other marine basins. The data gathered on experiments carried out are presented herein.

2. METHODOLOGY

For welding the joints we employed as base material the EH36BM naval steel sheets. The chemical characteristics of the utilized steel are given below, in Table 1.

Table 1. Chemical composition (%) of the EH36 steel

C	Mn	Si	P	S	Al	Nb	V	Ti	Cu	Cr	Ni	Mo
0.06	1.39	0.25	0.01	0.004	0.024	0.04	0.05	0.02	0.02	0.02	0.02	0.01

The MAG-M mechanized butt welding with metal-cored wire and rutile flux-cored wire in two welding positions, comfortable (horizontal PA) and inconvenient (PC) - Florescu *et al.*, 2018. The following materials were used in this experimental program: base material (high strength steel sheet EH 36, dimensions 300 x 150 x 10 mm), filler material (metal cored wire (E70C6MH4) and rutile flux-cored wire (E71T1MH4) according to AWS A5.18, with a diameter of 1.2 mm, as well as and auxiliary materials, such as M21 - Corgon 18 gas mixture and flat concave channel ceramic support. For both samples two stands equipped with the Phoenix 405 Progress pulse MM TDM universal welding source and the K-BUG 5102 welding machine were used.

During the welding of the samples, some of the technological parameters were kept constant: the stopping time on the edges, tsm = 0.2 ms; gas protection rate QG = 18 l/min; preparing time tpreg = 5 s; postgaz time tposg = 5 s and sample nozzle distance hd-p = 15 mm. The remainder was changed from one layer to another and from one welding position to another - Table 2.

After each welding of the samples, non-destructive (visual and RX 100%) and destructive (laboratory mechanical tests) were performed, the results being very good. To analyze the behavior of welded joints against corrosion, a sample of seawater taken from a depth of 5 m was collected by using the rossete sampler, equipped with Niskin bottles, available onboard of the marine research vessel *Mare Nigrum*. The coordinates of the probation station are N 44^{0}50’30.6“ and E 29^{0}45’31“. The water parameters from the site sampled are listed in Table 3.

Following mechanical laboratory tests, each individual welding has been tested for corrosion, samples being taken with compressed root from transverse bending. After sampling, one of the front surfaces of the specimens was rectified. Samples used in the experimental protocol were copper-bonded and epoxy resin isolated for obtaining a measurable area. Steel samples were degreased with alcohol and acetone. For the corrosion experiments, a three-electrode standard cell consisting of the tested samples have been employed as working electrode, a Pt-Rh network used as an auxiliary electrode and an Ag/AgCl electrode (saturated KCl solution, E = 200 mV *versus* normal hydrogen electrode - NHE) as a reference electrode. The experiments were performed using a PGZ 100 Potentiostat/Galvanostat. For the data record, the VoltaMaster 4 software has been employed.

Table 2. Parameters of modified welding modes.

Nr. row	Kind of layer	Type of welding wire	Transfer mode	v_e [m/min]	I_w [A]	U_a [V]	v_t [cm/min]
				v_p [cm/min]	L_p [mm]	v_s [cm/min]	E_l [KJ/mm]
PA							
1	root	Metal-cored wire (E70C6MH4)	RootArc	4.5	183	26.5	25
				80	6	10	0.065
2	final	Rutile flux-cored wire (E71T1MH4)	ForceArc	11	302	31	30
				80	8	13.7	0.091
PC							
1	root	Metal-cored wire (E70C6MH4)	RootArc	5.9	170	18.9	60
				-	-	60	0.071
2	filling	Rutile flux-cored wire (E71T1MH4)	ForceArc	8	220	25.3	60
				-	-	60	0.012
3	final			7	192	22.5	92
				-	-	60	0.009
4				6	167	18.9	60
				-	-	60	0.007
5				5.5	160	18.9	92
				-	-	92	0.004

Table 3. The sea water characteristics.

Depth	Pressure	Temperature	Sima-Theta	Salinity	Conductivity	Oxigen	Oxigen	Oxigen	Flurecence Seapoint	pH	ORP
m	db	˚C	Kg/m³	PSU	S/m	mg/l	μM/l	% saturation			mV
5	5.283	19.1141	10.0022	15.2983	2.22	10.48	327.69	128.49183	1.91	8.43	144.73

3. RESULTS AND DISCUSSION

3.1 OCP (OPEN CIRCUIT POTENTIAL)

Corrosion tests with open potential were initiated by monitoring the evolution of the open circuit potential after immersion in the test solution until they reached the stationary state. The potential-time measurement of the three different surfaces studied in natural sea water is shown in Fig. 1. The evolution of the OCP was monitored during 1 hour for each sample. The OCP trend of 36 mm uncoated EHG steel falls slightly down from 641 mV to -676 mV *versus* Ag/AgCl during immersion. Potential change to the negative direction indicates that this material is not able to form a protective oxide layer on its surface after exposure to marine environmental conditions, as shown by (Mardare & Benea, 2017).

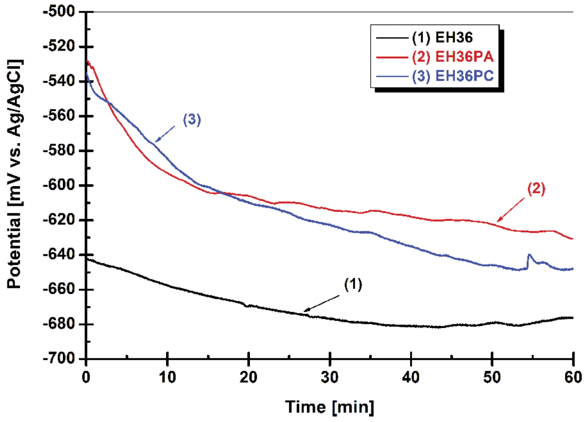

Fig. 1. Variation of open circuit potential with time immersed in sea water for: (**1**) EH 36, (**2**) EH 36 PA, (**3**) EH 36 PC.

For the EH36PA steel sample, the OCP continued to decrease during the immersion period, while the stationary potential was not reached. This potential of EH36 PA drops from a value of approximately -526 mV to - 626 mV *versus* Ag/AgCl. For the EH36PC steel sample, the OCP continues to decrease slightly during the immersion period by the end of the immersion period time, the value slowly rising from -535 mV to -648 mV *versus* Ag/AgCl; this modification associated with a good behavior at corrosion, yet the three samples show a similar rend, namely the inability to keep the oxide layer on the surface.

3.2. EVOLUTION OF POLARIZATION RESISTANCE DURING IMMERSION TIME

Evolution of polarization resistance was performed by the linear polarization method around the free potential with a very small potential difference (± 40 mV) to maintain the stationary surface. To note that the resistance to the linear polarization is the only corrosion monitoring method to measure corrosion rates directly, in real time. Our experiments show that the lowest value of polarization resistance (Rp) is reached by EH36PC steel (Fig. 2).

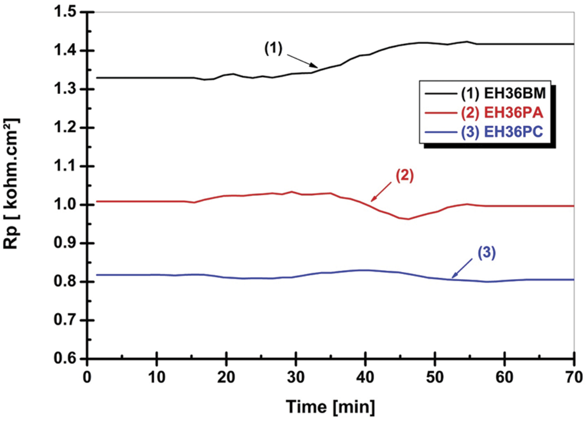

Fig. 2. Evolution of Rp values during the immersion period of: (**1**) EH 36 BM, (**2**) EH 36 PA, (**3**) EH 36 PC.

This Rp value for the uncoated EH36MB naval steel remains constant during immersion in seawater. For the EH-36PA welded joint sample, Rp has an average value of about 0.889 kΩ•cm^2, being larger than that of the EH36PC welded joint, for which we obtained a value of 0.754 kΩ•cm^2, which is significantly lower than for EH36MB with an Rp of 1.343 kΩ•cm^2.

The increased value of the polarization resistance means a lower density of corrosion current and therefore a lower corrosion rate, as it can be seen in Fig. 3. The upper corrosion current density corresponds to EH36MB.

According to the data presented in Fig. 3, it can be noticed that the higher corrosion rate, as the penetration rate, corresponds to the EH36MB naval steel, compared to two types of bending welded joints.

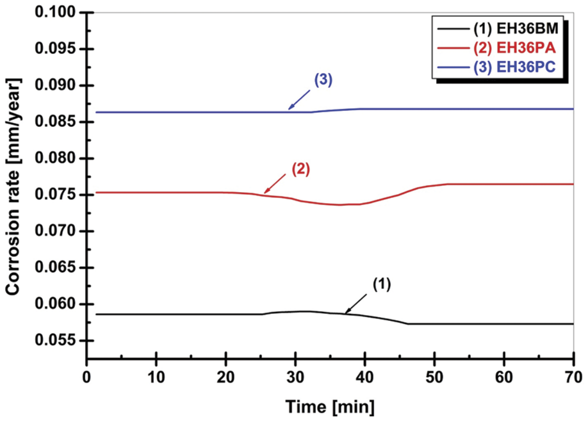

Fig. 3. Evolution of corrosion rate during the immersion period of: (**1**) EH 36 BM, (**2**) EH 36 PA, (**3**) EH 36 PC.

From the corrosion rate evolution, taking into account the penetration rate shown in Fig. 3, we identified for welded steel joints of EH36PA and EH36PC values of 0.076 mm/year and 0.086 mm/year that fit the welded joint EH36PC compared to that of single steel used as EH36BM base material, indicating a corrosion value of 0.057 mm/year. The values are equally sensitive. The results of the tests against the welded bending joints are coonsistent with the results of polarization resistence test.

3.3. POTENTIODYNAMIC POLARIZATION

The I = f (E) curves (potentiodynamic curves) were recorded and the potentials are ranging from -1500 mV to Ag/AgCl to +1500 mV *versus* Ag /AgCl at a scanning rate of 5 mV/s. Potentiodynamic polarization charts were performed for evaluating the corrosion performance of the EH36BM steel and the bending EH36PA and EH36PA welded joints (Fig. 4). In the aforementioned figure, a higher current density may be observed both in the cathodic and anodic fields for the steel used as the EH36MB base material, as for welded joints. For EH36BM EH36 steel base material, hydrogen reduction activity may be seen in the cathodic field and in the anodic field.

Due to the oxidation process, the passive film is destroyed and the current density increases to nearly 166 mA/cm^2, as shown in Fig. 4. For the welded joint of the EH36PA steel plate, the current density in the anode range reaches 168 mA, while the passive film is damaged approximately at a very appropriate value of the EH36MB base material.

Compared with EH36 steel, which is the EH36BM base material, the current density is higher for both EH36PA and EH36PC welded joints with a current density of 236 mV. The current density values for the two bending welded joints, which are very small compared to the EH36MB base material, show very good performance of the addition material and welded joints required for bending and the marine corrosive environment.

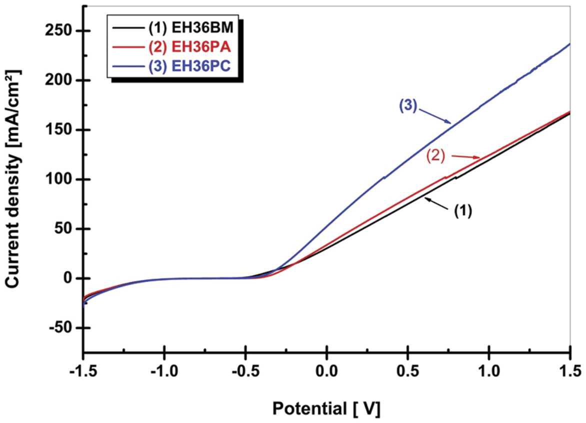

Fig. 4. Potentiodynamic polarization curves of: (**1**) EH 36 BM, (**2**) EH 36 PA, (**3**) EH 36 PC.

Higher current observed in the anode field suggests a general dissolution of the weld joint. The EH36PC welded joint has a higher corrosion rate than the EH36PA welded joint and the EH36MB base material. In the cathodic field, the passive film is destroyed by the hydrogen reduction reaction, while in the passive domain, the passive film is formed by the oxidation process. In the transposable domain, the passive film is damaged and dissolution occurs through passive film.

4. CONCLUSIONS

From the results gathered in the experimental research, we can conclude the following:

- Electrochemical analysis of samples taken from welded joints immersed in an aggressive environment shows a corrosion resistance almost similar to welded joints as well as for base material.
- OCP measurements of welded joints show noble potential compared to EH36MB steel base material. Additionally, the potential value of welded joints is more positive compared to the potential value of the base material.
- The corrosion resistance of bending welded joints, EH-36PA and EH36PC, has been studied by electrochemical methods. Electrochemical studies in natural seawater (at 25°C) have shown that the corrosion-resistant properties of bent and bridged welded joints have sensibly similar differences.
- The corrosive behavior of EH36 steel and the additives used in its welded joints are important for prior understanding and combat the marine environment corrosion.
- The performance of corrosion resistance in the marine environment of EH36 steel used as the base material and welded joints made by the MAG-M mechanized welding process; therefore, subject to bending is very good.

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