

POSSIBILITY OF CORROSION MONITORING RESISTANCE OF AUSTENITIC STEEL FOR SHIP CONSTRUCTION

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Abstract

The article presents the investigation results on possibility of electrochemical corrosion monitoring of the 1.3964 steel used for ship construction according of the patent PL 216723. The patent's assumption describes the method of on-line registration of electrochemical potential specifying the protective effectiveness of a thin oxide layer formed spontaneously on the steel surface. Essential drop of the potential's value with respect to the stationary one indicates layer cracking and initiation of pitting corrosion. Such a corrosion can be initiated by salinity and temperature of seawater and/or by a mechanical factor (strain). The carried out measurements of the potential and mechanical-electrochemical tests made it possible to determine the stress level causing the crack of oxide layer and initiation of corrosion processes in the steel. Thereby, the mechanical properties (R_m and A_5) thin passive oxide layers investigated steel. Application of Electrochemical Impedance Spectroscopy (EIS) in the laboratory allows monitoring of weakness (stratification) of the film as a stage preceding to fracture [1, 2]. Stress cracking of the protective oxide layer on the 1.3964 steel takes place beyond the exploitation zone (above the tensile strength) and there is no indication to monitor the corrosion resistance on ship construction made of this stainless steel. However, in specific cases when temperature of the steel exceeds 40°C, application of the monitoring may be justified.

Keywords: electrochemical corrosion, austenitic steel, monitoring

1. Introduction

In shipbuilding, metallic and non-metallic materials are being used, according to the requirements and recommendations of shipbuilders. Those materials must meet a number of requirements [4].

Among the materials selected for use in Marine environment where the primary requirement is resistance to corrosion, on well as where the appropriately reduced acoustic emission and electromagnetic signature decrease a vessel's susceptibility to naval influence mines and the probability of being detected by surveillance systems, non-metallic materials are frequently used, e.g. polyester-glass laminates for the minesweepers design 207. However, as indicated by common practice, for shipbuilding most widely selected steel are used. Non-ferrous materials as aluminum, titanium or copper alloys are used mainly for equipment and smaller construction [7].

As to the Hull steel, these are classified according to their properties onto ordinary steels (OS), quality steels (QS) and high-strength steels (H-SS). Generally, the H-SS are used for load carrying construction of hulls and superstructures of ships. The widespread use of steels follows from the fact that their mechanical properties can be easily modified by alloying additions (Cr, V, Ni, Ti, Nb, Al.) and/or by heat treatment, chemical agents, mechanical working or combinations thereof [2, 10]. Moreover, steel is the preferred material because of the cost, production and repair technology, fatigue strength and fire resistance. Only the production of small vessels from thin sheets may be problematic. Also the corrosion resistance of QS is lower in comparison with aluminium alloys and composites but most shipyards are using these steels, in particular for larger vessels, in order to avoid fatigue cracks, whereby the corrosion resistance is ensured by proper protection (open cathodic protection or passive protection with special protectors and sets of paints) [6, 7].

Some of marine construction materials as aluminium alloys or austenitic steels, owing to their physical and chemical properties, allow monitoring of their corrosion resistance by analysing the electrochemical parameters of passive films [8, 9]. These thin layers are created spontaneously on the surface of those materials in the form of an airtight film with high adhesion, which under certain conditions represent a natural effective corrosion protection. Its rupture or weakening under exploitation stress (strain) is indicated by a drop of the value of electrochemical potential with respect to the stationary one.

Until now, austenitic steels have been rarely used for ship constructions. Only the selected components of the minesweepers 207 were made of the stainless steel 1.4404. Currently, for hulls and superstructures of a series of these ships, the steel 1.3964 (EN 1.3964) was used [11]. Its choice was dictated by the purpose of these ships (destroying miners). This non-magnetizing steel allows significant reduction of physical fields of vessels made thereof and achievement of satisfactory corrosion resistance (up to 40°C) which follows from spontaneous creation of a thin passive protective layers on its surface [2, 8]. Physical and chemical properties of this oxide film (chromium oxide) prevent further oxidation of the steel. Mechanical properties of the layer are such that it is cracking under certain load (stress/strain) thus making further corrosion possible. The stress level resulting from static stretching recorded simultaneously with electrochemical potential (E) of the oxide layer allows, according to the assumptions of the patent 216723, to detect the stress level at which the corrosion processes are indicated. This fact is indicated by a significant reduction of the potential E [1]. If this phenomenon occurs in the range of exploitation loads (up to the limit of elasticity R_{sp}) it is justified to implement the aforementioned patent, i.e. to monitor the corrosion of newly built ships in such a way.

2. Testing methods and results

2.1. Sample preparation

Chemical composition of the steel 1.3964 (ISO 350) is given in Tab. 1. This is an austenitic stainless steel described by EN/DIN10088 acc. to WL). Its strength depends on the type of processing, which may consist of hardening or strengthening by cold setting, resulting in a high tensile strength level R_m of 700-950 MPa.

Tab. 1. Chemical composition of selected austenitic steels [4, 10]

Designation acc. to EN10088	1.3964		1.4539	1.4404	1.4039
Chemical composition	acc. to producer	acc. to the certificate	acc. to producer		
C %	max. 0.03	0.012	<0.02	<0.03	0.03
Mn %	4-6	4.42	<2	<2	2
Cr %	20-21.5	20.32	19-21	17.5	19
Ni %	15-17	15.46	24-26	11.5	14
Mo	3-3.5	3.15	4-5	2	3
Nb	max. 0.25	0.12	-	-	-
N	<0.11	0.305	<0.15	<0.11	<0.11
Fe %	rest	rest	rest	rest	rest
Si	-	0.36	<0.7		
P +S	max. 0.019 + 0.0004		max. 0.03+0.01 Cu 1.2 – 2		

For chemical composition of the steel 1.3964 according to the certificate, the PRE clearance ratio was calculated with the following formula (1):

$$PRE = \%Cr + 3.3\%Mo + 30\%N \tag{1}$$

$$PRE = 20.32 + 3.3 \times 3.15 + 30 \times 0.305 = 39.865$$

The higher the PRE ratio, the more resistant to pitting corrosion is the steel. In comparison with other selected steels, the steel 1.3964 has the highest PRE ratio (see the N-content) which may indicate the smallest susceptibility to pitting corrosion.

2.2. Corrosion testing and results

Determining of the stationary electrochemical potential of the oxide film on the tested steel was carried out in an artificial seawater of different NaCl – content and with addition of borate inhibitor. This inhibitor enhances the protective values are shown in Fig. 1 which was obtained by Data Logger with Software Communication Utility 3911 used to registration and elaboration of static data.

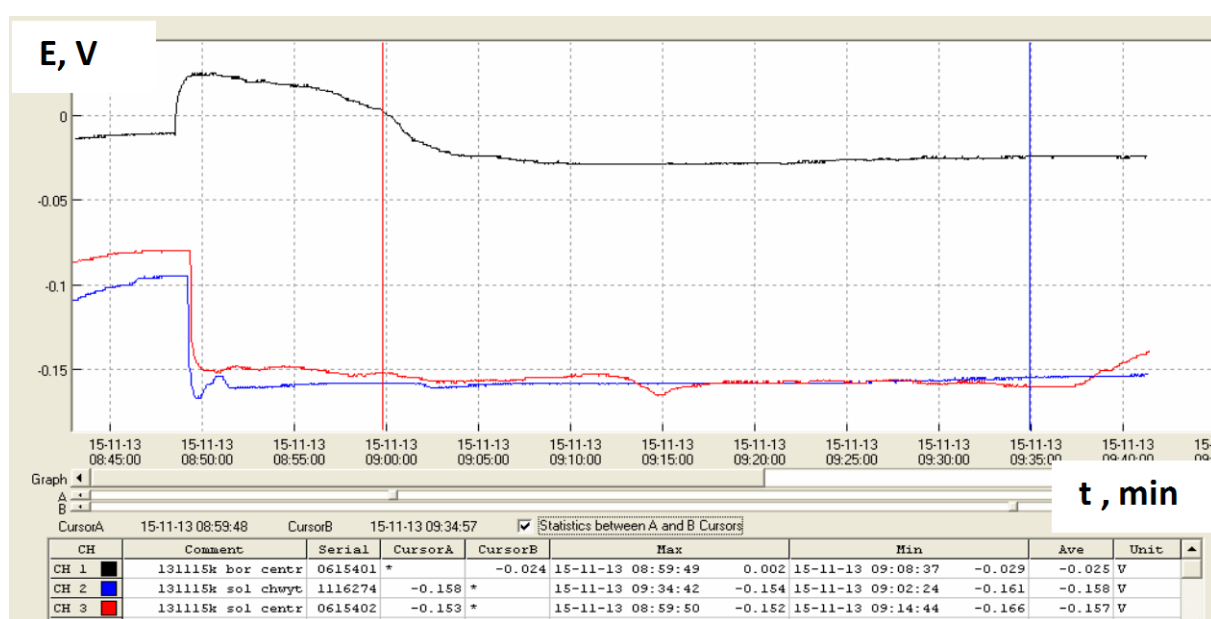


Fig. 1. Values of the stationary electrochemical potential E_{st} determined statistically in the range A-B for three types of corrosion factors: 1-water solution with 3.5% NaCl, 2-water solution with 1% NaCl, 3-water solution with 2 mM of NaCl and a borate buffer

Testing of mechanical and electromechanical properties of the steel 1.3964 was carried out in 3.5% NaCl aqueous solution (normalized artificial seawater) at ambient temperature 20°C. Further study of corrosion resistance of the steel was conducted in 1% NaCl aqueous solution (natural seawater, average sodium chloride concentration in the Baltic Sea) at temperatures of 20°C and above 40°C using silver-silver chloride (Ag/AgCl) electrodes. Practise shows that in summer the construction of ship superstructures can be heated up above the indicated limit temperature (>40°) which in the presence of fog brine (sea atmosphere) can cause corrosion of the constructions of new ships.

The values of stationary electrochemical potential for each type of corrosion factors were: $E_{st}=-157$ mV in 3.5% NaCl water solution, $E_{st}=-159$ mV in 1% NaCl water solution and $E_{st}=-25$ mV in 2mM of NaCl water solution with a borate buffer, which indicates that the lowest susceptibility to corrosion has the tested steel in a sea water solution with a borate inhibitor. At 20°C the concentration of NaCl in water has little influence on the value of E_{st} .

The susceptibility of the steel 1.3964 to pitting corrosion under influence of the above mentioned corrosion factors could be assessed in Fig. 2.

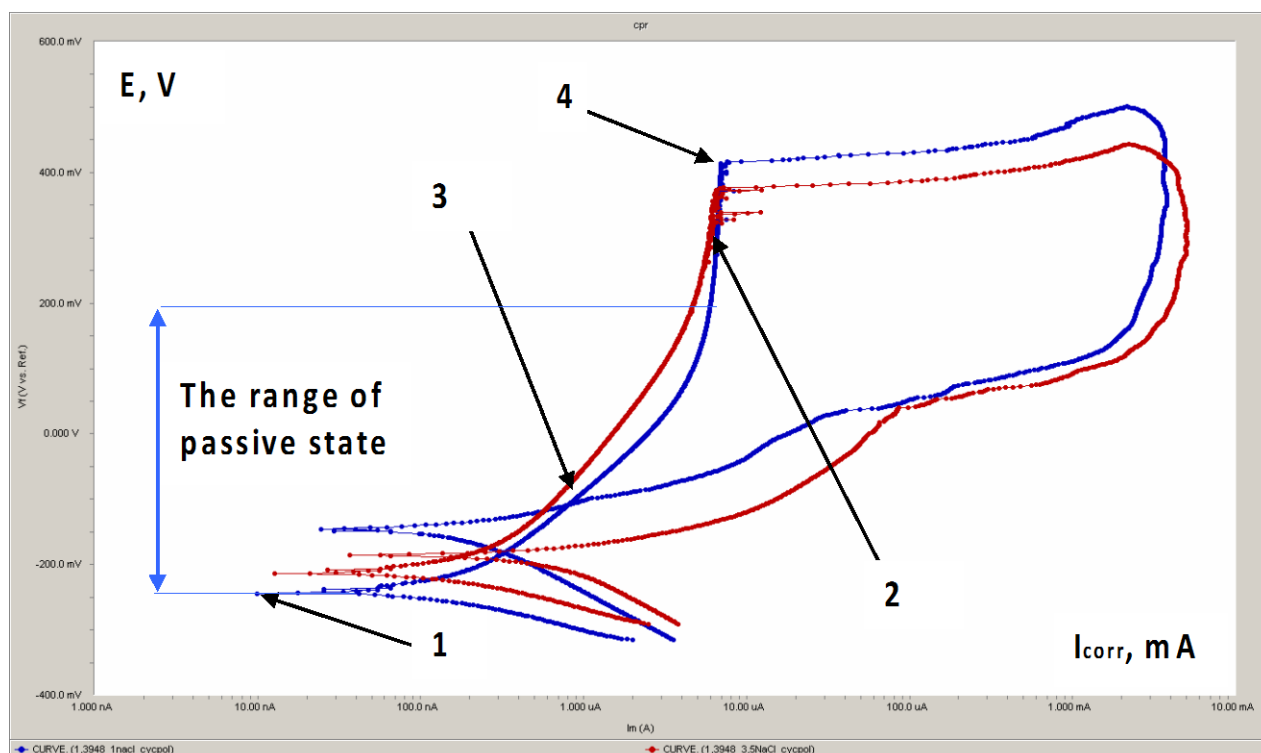


Fig. 2. Curves of cycling polarization of the 1.3964 steel in 1% NaCl water solution (natural seawater-blue) and 3.5% NaCl water solution (artificial seawater-red), where: 1-corrosion potential, 2-critical potential of pitting corrosion, 3-potential of repassivation of pits, 4-potential of nucleation of pits

Figure 2 shows the results of measurements obtained during cyclic polarization of the 1.3964 austenitic stainless steel in 1% NaCl water solution (blue curves) and in 3.5% NaCl water solution (red curves). The chosen solutions represent respectively the concentration of sodium chloride in the Baltic Sea and in ocean waters. The corrosion potential in both electrolytes is similar: it amounts to approx. -240 mV and -210 mV relative to the saturated calomel electrode (SCE). The scope of the passive extends up to the potential of about 300 mV, which is followed by approx. 100 mV range metastable corrosion, and intensive development of pitting corrosion. Smaller range of the passive state in the 3.5% NaCl solution proves its higher aggressiveness. When the potential exceeds 400 mV, intensive development of pitting corrosion takes place with significant increase of current (at minimal changes of the potential). In other words, the density of corrosion current becomes higher because the research was carried out on the samples of surface = 1 cm².

Such an examination of the steel 1.3964 was followed by static tensile tests aimed at determination of its mechanical and electro-chemical characteristics.

2.3. Mechanical-electrochemical testing and results

The static tensile test was conducted according to the methodology of simultaneous measurements of mechanical properties and electrochemical potential (at the same time and with the same frequency). In order to minimize the influence of disturbances, the gripped portions of the samples were isolated from the gripping jaws of the tensile testing machine. An extensometer installed on the measurement basis of $l=20$ mm gave an accurate reflection of the registered load in the initial stretching range. However, because of the excellent plastic properties of the tested steel (see Fig. 3) and large jaw stroke (up to approx. 58 mm), in the final stretching range the extensometer was taken off to eliminate its damage. The results of testing are shown in Fig. 3.

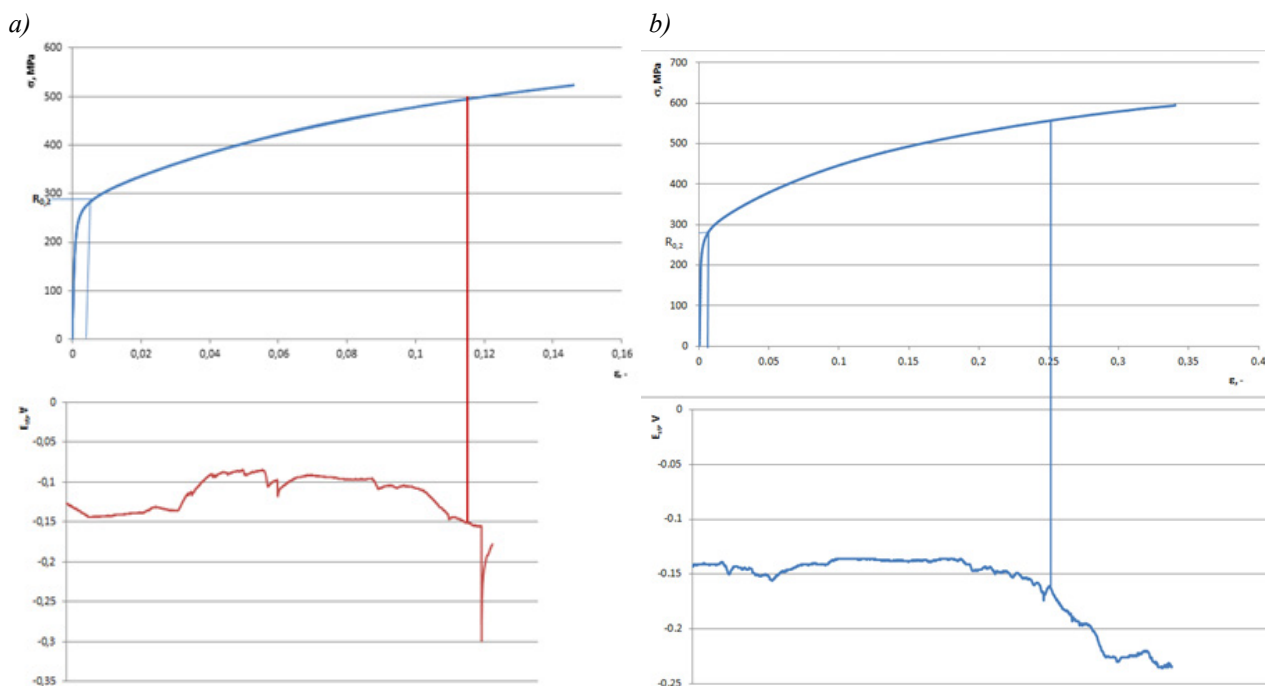


Fig. 3. Stress-strain (σ to ϵ) curves of the 1.3964 steel and the results of simultaneous measurements of electrochemical potential E of the oxide film on the surface of steel samples located in cells filled with: a) 3.5% NaCl water solution (artificial seawater), b) 1% NaCl water solution (natural seawater) relative to the Ag/AgCl electrodes at 20°C

In Fig. 3, the tensile strength is presented with causes cracking of the protective oxide layer. It is marked by a drop of the recorded electrochemical potential E . According to the patent PI 216 723, reduction of the stationary electrochemical potential E_{st} more than by 10 mV indicates the onset of the corrosion process. The registered in Fig. 3 stress (σ) and strain (ϵ) values for the steel samples are identical with those for the protective thin oxide layer. In the central part of the stretched sample /9 in the middle of the gauge length) the tensile stress is the protective layer and corrosion processes are initiated. The initiation of pitting corrosion occurs at the stress $\sigma=500$ MPa and strain $\epsilon=0.115$ (see Fig. 3a) which takes place at significant reduction of the electrochemical potential to $E=-300$ mV without repassivation. The phenomenon of repassivation, which consists in rapid reconstruction of the broken oxide layer, is marked by fluctuations of the measured potential. In the natural seawater, cracking of the oxide layer occurs at $\sigma=543$ MPa, $\epsilon=0.25$ (see Fig. 3b) and the repassivation is more intensive. It is seen that the differences in stress (strain) at which the cracking of protective layer on the tested steel is initiated follow from different concentrations of sodium chloride in water. Increase of the NaCl concentration in seawater at 20°C causes cracking of the protective layer and initiation of corrosion processes at lower stresses. That level of mechanical loads which is accompanied by cracking of the oxide layer the tested steel in 1% aqueous solution of sodium chloride is situated far outside the level of exploitation loads (stress up to 200 MPa).

According to the producer's certificate, the tested steel is susceptible to corrosion at temperatures above 40°C. Therefore, its testing was extended onto mechanical and electrochemical properties at 47°C, particular attention being paid to the elastic range. The results of this testing are presented in Fig. 4.

Increased accuracy of measurements enables to notice small fluctuations of potential value, which indicates that exploitation at temperatures above 40°C, may lead to minimal pitting corrosion with immediate repassivation. However, significant cracking of the preventive oxide layer at higher temperatures and corrosion occur only when the stress exceeds 345 MPa, which is far beyond the exploitation range.

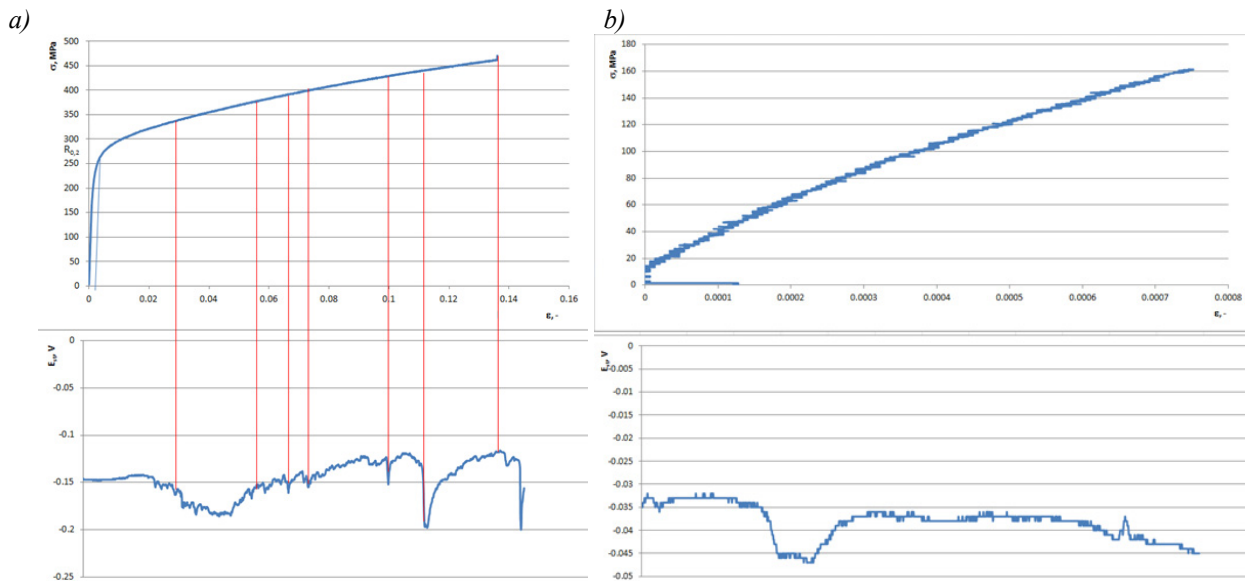


Fig. 4. Stress-strain (σ to ϵ) curves of the 1.3964 steel and the results of simultaneous measurements of electrochemical potential E (Fig. 4a) on samples in 1% NaCl water solution at 47°C

4. Summary

The steel 1.3964 of a composition given in Tab. 1, applied to constructions of hulls and superstructures of newly built ships, due to an extra addition of nitrogen ($N=0.305$) shows a high PRE ratio. This means good resistance to pitting corrosion. However, the results of cyclic polarization (Fig. 2) indicate that also at the corrosion potential lower than 0.4 V such a corrosion take place. Fluctuations of the corrosion current, which are related to the intensity of pitting corrosion, are small. Only at higher content of NaCl in seawater, these fluctuations are more intensive. Since the pitting corrosion of the tested steel occurs at ambient temperatures somewhere round 20°C, further testing at higher temperatures became unnecessary. Irreversible processes of pitting corrosion of the tested steel start up in 3.5% NaCl water solution at the corrosion potential $E=300$ mV and density of the corrosion current $j=8 \mu\text{A}/\text{cm}^2$, whereas in 1% NaCl water solution-at the corrosion current $j=10 \mu\text{A}/\text{cm}^2$.

On selected plots of static tensile tests in Fig. 3 and Fig. 4, it is seen that the stress range under exploitation loads is 200-250 MPa while the yield strength of the tested steel lies between 190 MPa and 210 MPa. Its tensile strength is relatively high ($R_m > 60\%$ at $Z > 50\%$). Generally, the experimentally determined mechanical properties of this steel are not as good as those properties given in the producer's certificate.

Electrochemical testing of the 1.3964 steel showed that the stationary electrochemical potential E_{st} (without load) ranges from -155 mV to -160 mV relative to silver/silver chloride (Ag/AgCl) electrodes. Minor differences of E_{st} (Fig. 1) in 3.5% NaCl aqueous solution (artificial seawater) at ambient temperature 20°C confirm ideal test conditions (without interferences). The borate inhibitor added to 2mM of NaCl aqueous solution for comparative purposes led to the lowest corrosion potential: -0.025 V relative to Ag/AgCl electrodes, which was the result of strengthening of the protective oxide film. However, the feasibility of using this reagent in the practice of corrosion prevention in marine environment is small; hence, the further tests were focused primarily on samples in 1% NaCl aqueous solution without inhibitors.

Advanced research of corrosion at cyclic polarization (Fig. 2) indicates the susceptibility of tested steel to pitting corrosion: the formation of pits occurs at $E=380$ mV. At $E=420$ mV the corrosion processes develop without repassivation (without reconstruction of protective layers).

Cracking of the protective oxide layer (initiation of corrosion) on the surface on the 1.3964 steel occurs, depending on the type of corrosion factor, under the stress ranging usually from

500 MPa to 550 MPa. To sum up, the cracking of protective layers and initiation of corrosion processes take place far beyond the real exploitation loads so that the monitoring of electrochemical potential on ship constructions fabricated from the 1.3964 steel is unnecessary. Only at higher steel temperatures ($>40^{\circ}\text{C}$) such a monitoring maybe justified.

5. Conclusions

From the study of mechanical and electrochemical properties of the 1.3964 steel applied for construction of a special-purpose craft it follows that:

1. The tested steel exhibits high strength properties ($R_m > 600$ MPa, $R_{0.2} > 285$ MPa) and extremely high plastic properties ($A > 60\%$, $Z > 50\%$).
2. Electrochemical testing of the unloaded steel shows its susceptibility to pitting corrosion at ambient temperature (20°C) regardless of the NaCl concentration in seawater, in spite of the high PRE ratio (~ 40) resulting from an extra addition of nitrogen.
3. Simultaneous interaction of seawater and tensile load causes corrosion of the test sample at stresses above 500 MPa or 550 MPa depending on the NaCl concentration (in an artificial or natural seawater), marked by debasement of the electro-chemical potential of the oxide film on the surface of test sample.
4. Increase of the temperature of 1% NaCl water solution (natural seawater) up to 47°C results in initiation of corrosion processes of the tested steel at tensile stress 345 MPa (comparing to 550 MPa at 20°C).
5. Increase of tensile load is followed by fluctuations of the electrochemical potential. Decrease of its value from -160 mV to -176 mV indicates weakening of the oxide film. Cracking of the film results in initiation of corrosion processes on the surface of test sample is marked by further decrease of the potential below -176 mV.
6. Temperature and salinity of seawater determine the stationary electrochemical potential. Its value is stabilized after 15 minutes.
7. Decrease of the potential value below -176 mV results from rupture of the oxide film, which causes corrosion of the sample. The cracking of this protective film starts up at tensile stress $\sigma = 550$ MPa and strain $\varepsilon = 0.25$ in 1% NaCl water solution (natural seawater) or at $\sigma = 500$ MPa, $\varepsilon = 0.11$ in 3.5% NaCl water solution (artificial seawater). These values of σ and ε refer both to the film and to the sample. According to the patent PL 216723, as the parameters to be monitored either σ or ε (strain gauge measurements) can be taken.
8. Monitoring of corrosion processes of ship constructions fabricated of the 1.3964 steel located within its elastic range is unnecessary.
9. At specific operating conditions the temperature of a construction (e.g. deck) can increase above 40°C when steels become susceptible to corrosion, which may justify monitoring of corrosion processes.

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