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## Influence of Stress-Corrosion Fractures on Potential of Ship- Building Metals in the Sea Water

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### Abstract

The installation for newformed surface creation of the metal has been developed. Experiments were carried out in model solutions of NaCl on samples of various shipbuilding metals. Shipbuilding metal potentials without oxide film in the marine and ocean water have been obtained. The results show how much the steel potential value were critical "inside" the crack under corrosion-mechanical and fatigue destruction. The obtained results show that the electrochemical corrosion account is possible at application of high-tensile steels, which used in dynamically loaded constructions in corrosion environments. Investigation of the steel protection parameters in relation to specific products and service conditions may allow to control the corrosion fatigue properties of metals and predict this characteristics in the future.

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*Keywords:* stress-corrosion fractures; metal potential; oxide films; cathodic protection; sea water

### Nomenclature

NaCl	chloride of sodium
$\varphi$	the electrochemical potential of metal, V
t	the period of experiment, s
L62	brass

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St3	structural carbon steel
09G2	structural alloy steel
20Cr13	rust-resisting steel
AMg15-61	aluminum-magnesium alloy

## 1. Introduction

Today the problem of stress-corrosion fractures (corrosion cracking and corrosion fatigue of steel) is primary on ocean vessels and structures operation [1]. This particularly occurs during the weather conditions impairment. So that during a violent storm 10 – 11 November 2007 in the Kerch Strait the several bulkcarriers sank, the tanker split in two parts, about 1300 tons of oil fuel and 6,800 tons of sulfur were dropped into the sea. In the whole 20 ships transferred SOS signals. At the same time a lot of damage was done to the buildings and coastal promenade in Sevastopol. Such natural phenomena occurs in the Azov and Black Sea every few years [2]. Reference [3] is concerned with the automation of coastal promenade protection from destruction.

Lowering of the corrosion-fatigue strength, corrosion fatigue and hydrogen embrittlement negatively affects metals in seawater during the operation, and thus leads to large economic losses. Also, the surface strength losses increase on 15...20% due to the Rebinder effect [4].

The surface layers play a special role in fatigue, as microcracks are formed on the free metal surface which is the course of destruction.

Corrosion fatigue is the defect and failure of metals under the action of cyclic stresses and corrosive environment. Such combined effect exacerbates the work of structural alloys in products, reducing their durability fatigue life and fatigue limit. Sea and river transport, power-engineering, oil and gas production and etc. industries bear large losses of corrosion fatigue. Influence of corrosive environments is receiving increasing attention to enlarge the strength requirements used in alloys engineering [5].

Stress-corrosion cracking is one of the most dangerous and practically important types of damage and their destruction under the combined effect of statically applied stresses and active environments.

Impressed current electrochemical cathodic protection is the most reliable and cost-effective way to protect against corrosion and mechanical damage underwater hulls of vessels and ocean structures. In most cases cathodic protection does not require it replacement during the life of the vessel (ocean structure) and provides optimum protection of the hull in different environments. For new designed vessels the cathodic protection reduces weight by eliminating the increased plate thickness on the amount of corrosive wear [6].

Cathodic protection from the external power source is performed by shifting the electrode potential of the protected metal surface into electronegative side. To ensure reliable protection the entire surface is required to set the value of the electrode potential on 0.1 V more negative than the potential of the material. So that the magnitude of protective current density reaches values of 0.2...0.3 A/m<sup>2</sup> [7]. However, in practice, these parameters do not provide adequate protection, especially in the presence of local destruction and corrosion fatigue, namely, there is not a complete protection against corrosion or overprotection causing corrosion cracking and other types of local damage.

## 2. Materials

Determination of metal potential "inside" a crack or other local defect is an important factor to prevent their development. Earlier attempts were made to determine the metal potential "inside" the crack. For example, it was proposed to use a tensile testing machine which is allowed to break the bar and measure the potential in the point of rupture [8]. Precise the potential measurement was difficult, it was made by a provision for the rapid formation of an oxide film on the bar crack surface. According to value of an oxide films on a metal surface presence, an installation for newformed surface creation of the bar (Fig. 1) has been developed on the Ocean Technology and Shipbuilding chair of Sevastopol National Technical University. This installation allows to conduct electrochemical characteristics explorations of metals without surface films.

Fig. 2 is the devices connecting diagram for the experiment. Engine, having different rotational speeds, feeds from direct current power supply Lab Tools 30V / 15A (1) – it is a pulse converter mains voltage regulated direct current output voltage, with a maximum regulated current up to 15A. The installation for newformed surface creation of the bar (2) allows continuous peel the investigated bar of metal (3). Measuring the potential of the metal is defined relating silver-chloride reference electrode (4) with the use of voltmeter (5). One-coordinate recorder N-307/2 (6) allows to schedule of the investigating process.

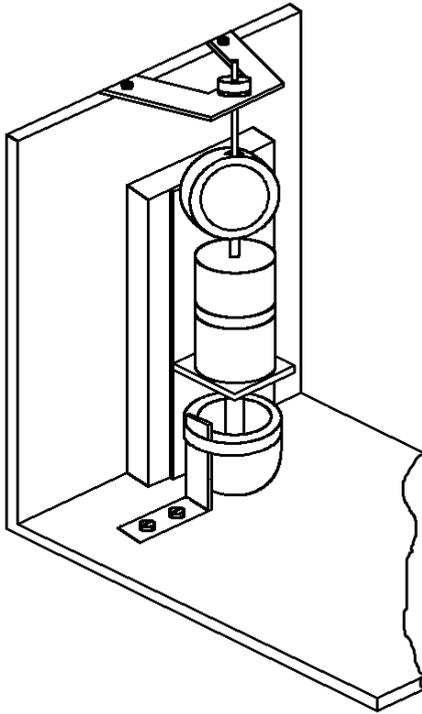


Fig. 1. Installation for newformed surface creation of the bar.

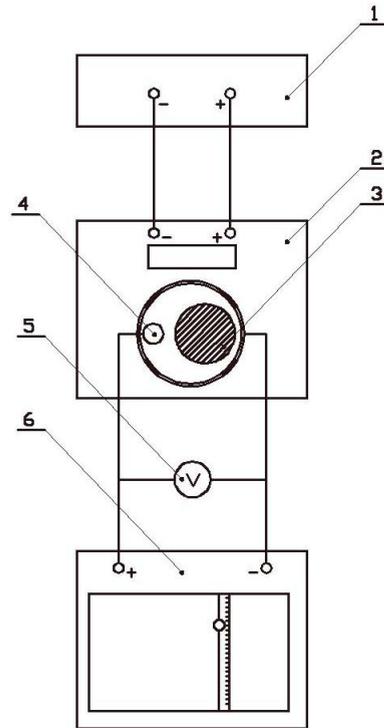


Fig. 2. The devices connecting diagram for the experiment.

A modern industry, including shipbuilding, applies a wide range of metallic materials with a wide variety of physical and physicochemical characteristics: carbon, low-alloyed and alloyed, rust-resisting steels, copper-alloy, aluminum alloys, etc. To conduct the investigations were selected representative bars of each steel groups and non-ferrous metals. We used the following bars of: brass L62; structural carbon steel St3; structural alloy steel 09G2; rust-resisting steel 20X13; aluminum-magnesium alloy AMg15-61.

Manufacturing technique of the bars (Fig. 3) provide reliable pressurization of non-working surfaces (1). Bars are isolated from the electrolyte by ink EP-755 to create only one working surface (2) and constitute a disk with a diameter of 25 mm ( $0.002 \text{ m}^2$ ) and a thickness of 3-4 mm and attached thereto a connecting stem (3) and contact lead terminal (4). Before starting the experiment, the bars are sandpaper to remove corrosive bloom and then grind and degreased.

To determine the potential of the investigated metals was chosen silver-chloride reference electrode (Fig. 4) [9, 10].

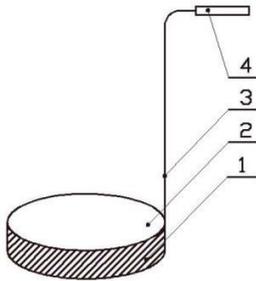


Fig. 3. Physical configuration of metal bar.

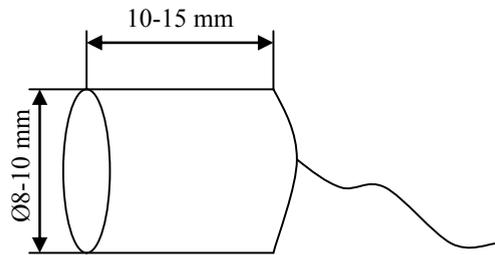


Fig. 4. Silver-chloride reference electrode

Silver-chloride reference electrode potential relative to the hydrogen electrode at room temperature is +200 mV.

### 3. Methods

For experiments used a model solution of NaCl in distilled water, this solution was simulating seawater. Investigations were carried out in NaCl solution with a concentration of 1.8%, which conform to a salt concentration in sea water and NaCl solution with a concentration of 3.0%, which conform to the concentration of salt water in the ocean.

The first part of the experiment was carried out as follows: the bar was immersed in a cell with the model solution, and then it was kept at it for a while, because when exposed to seawater metals are covered by a thick layer of fragile corrosion products. Therefore, we investigated the effects of corrosion on the potential of the metal with an oxide film.

Research the potential changes of the metal in sea water without the oxide film, that is "inside" a local defect, was possible by the installation for newformed surface creation of the bar (Fig. 1). Therefore, the second part of the experiment was into removing bar oxide and surface films. At the end of the experiment, after the termination of the installation, the recovery of surface and oxide films took place.

Throughout the experiment, we measured the potential and schedule.

There were conducted ten experiments, each metal was investigated in two model solutions.

### 4. Results and discussion

In the NaCl solution with a concentration of 1.8% (Fig. 5) the potentials metal with the oxide film are follows:  $\varphi$  (L62) = - 245 mV;  $\varphi$  (St3) = - 539 mV;  $\varphi$  (09G2) = - 557 mV;  $\varphi$  (20Ch13) = - 242 mV;  $\varphi$  (AMg15-61) = - 768 mV.

In the process of removing surface films, potential values change rapidly, and are range within:  $\varphi$  (L62) = - 512 mV;  $\varphi$  (St3) = - 389 mV;  $\varphi$  (09G2) = - 469 mV;  $\varphi$  (20Ch13) = - 578 mV;  $\varphi$  (AMg15-61) = - 1 111 mV.

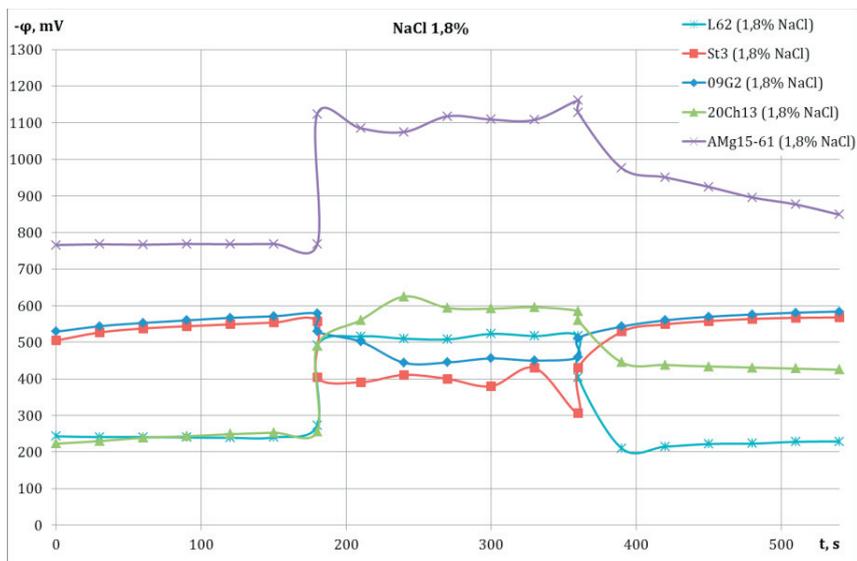


Fig. 5 Graphical representation potential gradient metals bars in 1.8% solution of NaCl.

In the NaCl solution with a concentration of 3.0% (Fig. 6) the potentials metal with the oxide film are follows:  
 $\phi$  (L62) = - 264 mV;  $\phi$  (St3) = - 530 mV;  $\phi$  (09G2) = - 528 mV;  $\phi$  (20Ch13) = - 167 mV;  
 $\phi$  (AMg15-61) = - 644 mV.

In the process of removing surface films, potential values change rapidly, and are range within:  
 $\phi$  (L62) = - 510 mV;  $\phi$  (St3) = - 487 mV;  $\phi$  (09G2) = - 486 mV;  $\phi$  (20Ch13) = - 472 mV;  
 $\phi$  (AMg15-61) = - 1195 mV.

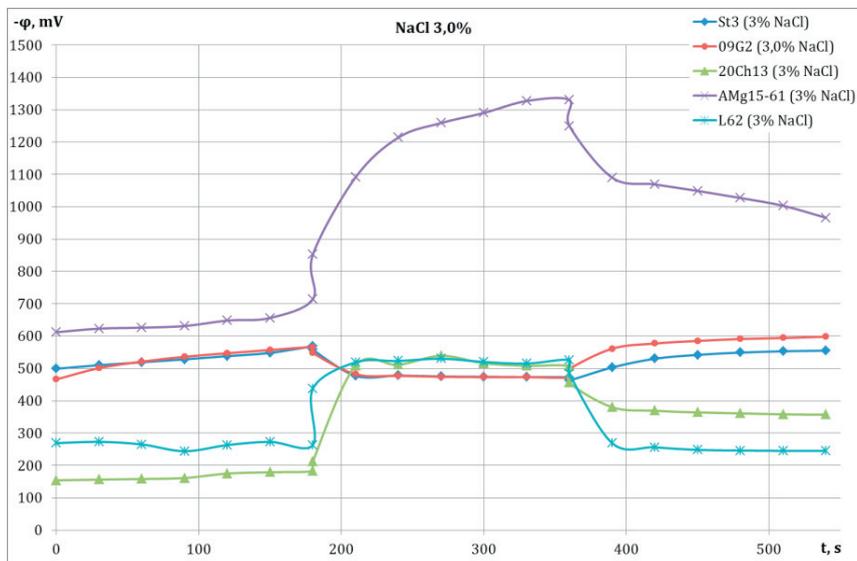


Fig. 6 Graphical representation potential gradient metals bars in 3.0% solution of NaCl.

When the newly formed surface in the process of bar sanding, the metal begins to interact with the environment actively. As the results of the experiments series show, the continuous removal of surface and oxide films with St3 and 09G2 bars cause the electrode potential offset in the positive direction, which can be explained by inhibition of the oxidation process on the surface and also by the mechanical removal of the adsorbent from the metal surface.

The results of experiments obtained by removing the surface film of rust-resisting steel 20Ch13 spark the particular interest. The potential value of this steel approaches to the negative side, and in 3.0% NaCl solution with an some error equal to the potential of other investigated steels. This phenomenon can be explained as following. A characteristic feature of the rust-resisting steels is the rapid formation of a passive oxide film which protects the surface of the steel from corrosion. Due to the installation effects on the surface of the steel – the oxide and surface film are destroyed and therefore the steel loses its corrosion-resistant qualities.

Aforementioned assumptions are applicable to brass and aluminum-magnesium alloy, which are characterized by the presence of passive surface films.

After end the removal of surface and oxide films the potential of all bars approaches to take the starting value. This is due to repeated adsorption of chloride ions from the electrolyte to the metal surface, and formation of recondition double-electric layer at the metal-electrolyte interface.

As a consequence, previously unknown phenomenon revealed after a series of experiments it was found out that – potential both carbon and rust-resisting steel in the formation of newly formed surfaces have the same characteristics "inside" the local defects, i.e. during cracking, despite differences in metal crystal lattice, mechanical properties and chemical composition, they have similar properties. In the other words, it is possible to revision the existing views on the use of strong and rust-resisting steels in aggressive environments, if damage the surface and oxide films is possible, as well as in anaerobic environments, due to the inability of passive oxide films, for example in an environment of hydrogen sulfide in the operation of offshore structures in the Black Sea.

On the basis of the foregoing, it can be concluded that the offset potential while sanding largely due to adsorption of ions from the electrolyte solution. During the preparation of the newformed surface adsorption of charged particles from the solution is complicated, and the electrode potential of the metal does not change. The results show how much the steel potential value were critical "inside" the crack under corrosion-mechanical and fatigue fracture of steels both in air and in seawater with polarization.

## Conclusion

The opportunity to research metals without surface and oxide films are received, it was possible to study the metals behavior "inside" of the crack.

The results show how much the steel potential value were critical "inside" the crack under corrosion-mechanical and fatigue destruction. The obtained results show that the electrochemical corrosion account is possible at application of high-tensile steels, which used in dynamically loaded constructions in corrosion environments. Hereof also follows that steel polarization potential for a cathodic protection from local fractures is necessary to define on newformed surface.

The observed phenomenon immutability potential of the metal with a minimum of surface charge on the newformed surface has important theoretical and practical significance for electrochemical protection from corrosion and mechanical fracture of vessels and ocean structures.

Investigation of the steel protection parameters in relation to specific products and service conditions may allow to control the corrosion fatigue properties of metals and predict this characteristics in the future.

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