EURASIAN PHYSICAL TECHNICAL JOURNAL

2024, Volume 21, No. 1 (47)

https://doi.org/10.31489/2024No1/38-48

Received: 07/01/2024 Revised: 07/02/2024 Accepted: 11/03/2024 Published online: 29/03/2024

Research Article

**UDC: 539.232; 620.193**

# REASON OF PITTING CORROSION OF MARTENSITIC STEEL IN SEA WATER

Baikenov M.I., Seldyugaev O.B., Guchenko S.A., Afanasyev D.A.*

E.A. Buketov Karaganda University, Karaganda, Kazakhstan
**Corresponding author: a.d.afanasyev2@gmail.com*

***Abstract****. The assumption that corrosion of products from X17 martensitic stainless steel in seawater occurs due to incomplete oxidation of chromium atoms in cells on the surface of the products is made in the presented work. Incomplete oxidation of chromium atoms occurs in the cells of X17 steel. This is due to the fact that oxygen molecules at temperatures up to 350 °C not having enough energy for chemical interaction with trivalent chromium atoms entering the cubic body-centered cells of martensitic stainless steel. There is a significant decrease in the corrosion rate after placing X17 stainless steel products in 5% iodine solution in ethanol after pre- treatment of the product surface with active forms of oxygen. The treatment was carried out during 12 hours with chemically active forms of oxygen (ozone and singlet oxygen) at a temperature of 350 °C. Most of the chromium atoms on the surface of X17 steel samples were completely oxidized as a result of 12 hours exposure to highly active forms of oxygen. The density of the oxide passivation layer on the surface of the products increased significantly as a result of the formation of new bonds CHROMIUM - OXYGEN - CHROMIUM. This resulted in increased corrosion resistance. The rate of interaction with an alcohol solution containing halogen ions was reduced by 71% for the samples with the oxide passivation layer compared to samples of untreated X17 steel.*

**Keywords:** carbon steel; seawater; localized corrosion, oxidation, halogens, body-centered cubic structure.

## 1. Introduction

The big problem of intensive corrosion exists in the operation of metal products. It happens when metal products are exposed to seawater or marine climate conditions. For example, products made of ordinary carbon steel are very quickly destroyed even being on the shore under the condition of regular fogs coming from the sea [1, 2]. The construction steel St3 (steel 3), the analogue of which is produced in the USA under the brand name A57036. For this reason, stainless steels are commonly used for seawater applications. These steels are significantly more expensive than conventional carbon steels. In addition, not all stainless steels are equally well preserved in seawater. X18H9T (steel composition: 18% chromium, 9% nickel, 1% titanium), X19H9T (steel composition: 19% chromium, 9% nickel, 1% titanium) and X24H9T (steel composition: 24% chromium, 9% nickel, 1% titanium) steels with chromium content more than 18% and additionally alloyed with nickel have high corrosion resistance in seawater [3, 4], but these steels are quite expensive. For instance, a kilogram of X18H10T steel costs 4.2 US dollars (USD). Cheaper stainless steels with chromium content from 10.5% to 17% chromium (mass percent) [3] are much cheaper than steels with chromium content over 18% and the presence of other alloying elements. A kilogram of 08X17T steel costs 2.55 USD. However, these steels are highly corrosive in seawater. Although the corrosion resistance of X17 type steels is much higher than that of ordinary carbon steels [4]. In this regard, the surface of stainless steels with mass fraction of chromium less than 18% is often covered with a film of protective coating not sensitive to seawater. However, the creation of such coatings leads to additional increasing of the cost. The steel is coated with a layer of chromium, but this is a complex and expensive operation. 1 kilogram of pure chromium powder costs 130 USD. The development of cheap methods to increase the surface corrosion resistance of stainless steels with a chromium content of less than 18% is very relevant.

Much attention is constantly paid to the study of metal corrosion processes. This is evidenced by a large number of new articles [5-10]. Work is underway both to study the corrosion process of carbon steels [5-7] and martensitic steels [8-10]. The main methods for studying corrosion processes include electrochemical research methods [5, 6, 10] and electron and optical microscopy [5, 6]. A number of works have proposed new research methods [6, 7]. The significant role of the tribological characteristics of steels in the corrosion process was showed in [7]. Despite significant efforts aimed at studying corrosion processes in steels, a large number of issues remain that require consideration. Models of metal corrosion processes are still being discussed.

The article [11] shows that corrosion of aluminium in seawater occurs when the surface of products interacts with negative halogen ions. Seawater is actually a mixture of aqueous solutions of negative halogen ions. The article concluded that corrosion of aluminium in seawater is due to insufficient oxidation of aluminium cells on the surface of aluminium products. It was shown that incomplete oxidation of aluminium cells (42 % of the total number of aluminium atoms in the cells on the surface of the products have no covalent bond with oxygen atoms) is caused by the lack of energy of oxygen molecules under normal conditions (T = 0 °C, P = $10^5$ Pa, the concentration of oxygen 19-21% by volume). It was shown that complete oxidation of aluminium cells leads to the creation of a cell structure in which each aluminium atom in the cells is chemically bonded to three oxygen atoms. This eliminates the possibility of chemical interaction of aluminium atoms in such cells with negative halogen ions (i.e. the process of aluminium corrosion in seawater becomes impossible). The introduction of additional oxygen atoms inside the aluminium cells mechanically blocks the possibility of ion penetration inside the structure of aluminium products. In other words, the formed monolithic layer of corundum on the surface of the product is a barrier to the penetration of halogen ions into aluminium cells with not fully oxidized structure.

For conducting experiments to determine the corrosion rate of aluminium, a 5% solution of iodine in ethanol was used in [11]. The use of iodine is due to the fact that alcohol solutions of iodine are industrially produced. They are certified by state standards, they are not expensive, and these iodine solutions are relatively safe when conducting experiments. The opposite of this, fluorine and bromine solutions are highly toxic.

In this work, the possibility of increasing the corrosion resistance of stainless martensitic steel products, on the example of X17 steel, by method of additional surface oxidation is studied.

## 2. Materials and experimental details

There were 9 atoms in the unit cell model of X17 stainless steel for calculations, which 8 iron atoms and 1 chromium atom were present. Chromium was located in the center of the body-centered cubic lattice. Experiments were carried out with various samples of untreated and treated X17 stainless steel (16 wt% chromium content), with samples of untreated and treated St3 structural steel (US analogue A57036), with samples of treated and untreated chromium with 99.99% purity. All these samples were placed in 5 wt% iodine in ethanol. Experiments with 2.5 wt% iodine in ethanol and with 2.5 wt% iodine in water-ethanol mixture (50 wt% water and 50 wt% ethanol) were also carried out.

The mass of the samples before and after placement in the solution was measured on a RADWAG AS 60/220.R2 with electronic scale. The measurements were carried out to an accuracy of ten thousandths of a gram. There were used samples of X17 stainless steel, stainless steel X19H9T, structural steel St3, pure chromium and chromium with oxidized surface. The samples and the air entering these samples were heated to a temperature of 350 °C with simultaneous irradiation of the incoming hot air by ultraviolet radiation (UVT - ultraviolet treatment) of the DRT-400 lamp. DRT-400 lamp emits ultraviolet radiation in the range from 220 nm to 340 nm.

Elemental analysis of steel was carried out using an energy dispersive detector (EDX, INCAPentaFET-x3, Oxford Instruments, England) included in a scanning electron microscope (MIRA 3LMU, TESCAN).

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The surface properties of the films were investigated using a HV1000 hardness tester optical microscope. Microphotographs were taken at 160x or 400x magnification over the entire area of the specimen. The average pitting grain size was determined using the ImageJ program.

## 3. Results of theoretical and experimental research

Under normal conditions, an oxide film consisting of two subsystems is formed on the surface of stainless martensitic steel: iron oxide subsystem and chromium oxide subsystem with a thickness of 4 nm (Figure 1) [12]. Taking into account that the length of the face of a body-centered cubic cell of martensitic steel is 0.3 nm, no more than 13 layers of martensitic steel cells are placed in the passivated layer.

An assumption was made taking for stainless martensitic steels with chromium content from 10.5% to 18% into account the results stated in [11]. It is possible to increase the corrosion resistance of the existing oxidized layer for these types of the steels. The corrosion resistance of the hardened oxidized layer should significantly exceed the chemical resistance of the passivated layer on the surface of untreated martensitic steel. The basis for this assumption is the known fact that the main alloying component of stainless steels chromium atom can have a variable valence from 2 to 6 [13]**.** Chromium atoms have mainly valence 3 in stainless steels with the content of chromium less than 18%, but at the same time some chromium atoms on the surface of these steels have valence 6 [14]. It is still possible to increase the valence of most of the chromium atoms on the surface of stainless-steel samples up to 6 under the appropriate energetic influence on the structure of stainless-steel cells. On each chromium atom two or three additional covalent bonds with oxygen atoms (limiting valence 6) can appear at access of high-energy forms of oxygen. In this case, these oxygen atoms form a second covalent bond either with iron atoms or with other chromium atoms in a given stainless steel cell or in neighboring cells. One possible bonding scheme of trivalent chromium atoms in a stainless-steel cell located on the surface of the product at chromium content from 11% to 17% is shown in Figure 1. All atoms of one stainless martensitic steel cell are shown in full. In addition, the interaction of a chromium atom in a given cell with chromium atoms in neighboring cells is shown schematically. The interaction of chromium atoms occurs through oxygen bridges.

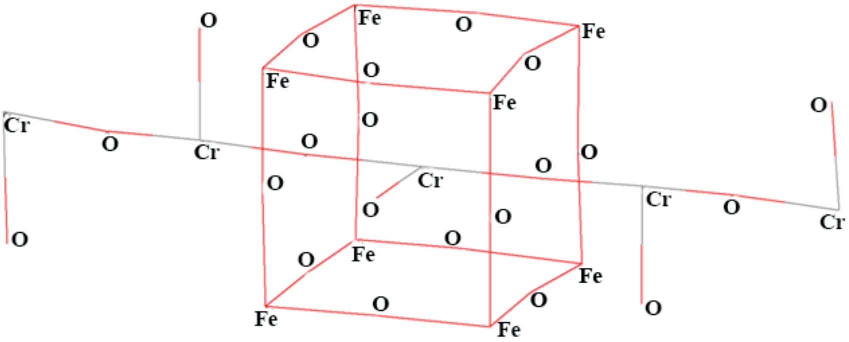

**Fig.1.** Scheme of possible arrangement of chromium and oxygen atoms in the cell structure on the surface of stainless steel with chromium content from 11 to 18%. Valence of chromium atoms 3.

Theoretical the concentration of 11% chromium at the stainless-steel cell is corresponding to one chromium atom in each stainless-steel cell with uniform distribution of atoms.

The martensitic steel cell is cubic body-centered and has 9 atoms, one of these atoms in the center of the cell [14]. Occurrence of chromium oxide films linking neighboring cells with each other as shown in Figure 1 is possible when the chromium atom is localized in the center of the body-centered cubic lattice. It should be realized that 11% is the average concentration of chromium atoms taking into account all stainless-steel cells. Whereas in a real alloy, the chromium atom may be absent due to the random distribution of chromium atoms in some cells. As a result of iron-chromium alloys are a system with unlimited solubility. These alloys conform to the three Hume-Roseri rules [15, 16]:

1. Close structure of valence shells of atoms of alloy components;
2. The presence of crystal lattices of the same type in the alloy components;
3. The difference in the size of atoms of the alloy components is not more than 8%.

The sizes of chromium and iron atoms differ by less than 8 %. The covalent radius of iron is 1.16 A, chromium is 1.22 A, the metallic radius of chromium is 1.28 A, iron is 1.26 A [17, 18]. In addition, typically, chromium has valence 3 in alloys, as do iron atoms. Due to the unlimited solubility of chromium in iron with an average chromium content of 11-17 % some cells may have two chromium atoms each. For instance, one chromium atom is located in the center of the cell and the other chromium atom is localized in a node of the crystal lattice and in some cells, chromium atoms will be completely absent. Cells in which chromium atoms are completely absent consist only of iron atoms. These cells will be the centers of corrosion and will be the first to break down when exposed to aggressive media (e.g. seawater). In steel, some cells do not contain a chromium atom, even theoretically if the chromium concentration is less than 10.5 %. These metals do not have a protective oxide film. As a result, the corrosion rate of a product made of this steel will be significant. Theoretically, at least half of the steel cells are missing chromium atoms in X5 steel with 5% chromium content. There are not enough chromium atoms for half of the cells. The appearance of a continuous oxidized chromium film on the surface is impossible. The number of cells that by chance may not contain a chromium atom decreases as the concentration of chromium in stainless steel increases from 11% to 18%. The number of cells unprotected from corrosion in the chromium oxide film on the surface of chromium-doped steel decreases. The significant increase in the corrosion resistance of stainless steel at a chromium content of 18 % is probably due to the fact that, starting from this concentration, at least one chromium atom is guaranteed to be contained in each stainless-steel cell. That is, there are no holes in the outer oxidized chromium film on the surface of the stainless steel product. This is schematically presented in the form of the figures where white squares represent cells not protected from corrosion, black squares represent cells protected from corrosion (Figure 2).

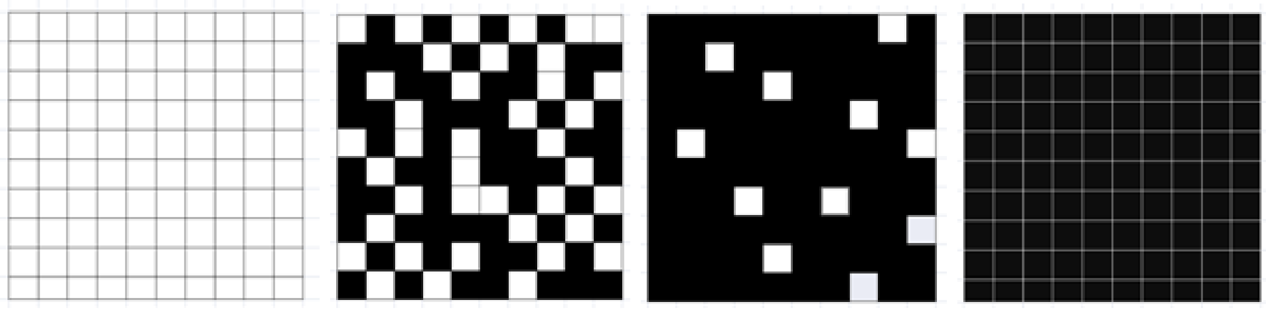
a) b) c) d)

**Fig.2.** Schematic representation of corrosion resistance of steel surfaces depending on chromium concentration (white squares represent cells not protected from corrosion): a) St3 (chromium 0,3 mass % ); b) stainless steel with 11 % chromium content (Large unprotected zones are observed in the structure of the chromium oxide subsystem); c) stainless steel with 17 % chromium content (Pointed unprotected defects are observed in the structure of the chromium oxide subsystem); d) stainless steel with 18 % chromium content (significant corrosion reduction is observed [4]).

Chromium atoms in unit cells of stainless martensitic steel can form additional 2-3 chemical bonds mainly with chromium atoms located in neighboring cells under the influence of high-energy forms of oxygen. The transition of chromium atoms from the trivalent state to the hexavalent state is a consequence of this process. The number of additional bonds of chromium atoms with iron atoms should be insignificant, since iron atoms always exhibit valence 3. Oxidation of iron atoms in the surface layer occurs already during the manufacture of the product, and in the surface layers of stainless steel there are no iron atoms capable of establishing new bonds with chromium atoms.

The establishment of new bonds within the stainless-steel cell will result in the strengthening of the cell itself. The additional CHROMIUM - OXYGEN - CHROMIUM bonds formed within the stainless-steel cells will mechanically block the access of halogen ions and protons to the IRON - OXYGEN - IRON bonds. Protons are the main component causing corrosion in fresh water as opposed to seawater. These protons are formed in any water by dissociation. In pure water and neutral solutions, the concentration of protons $[H+]=10^{-7}$ g-ion/l [19]. The scheme of possible bonds of hexavalent chromium atoms in stainless steel cells located under the first layer of the product surface at a chromium content of 17% is shown in Figure 3.

A significant increase in the density of CHROMIUM-OXYGEN bonds inside stainless steel cells is observed when comparing Figures 1 and 3. The chromium in the hexavalent state is located in the inside

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stainless-steel cells. That is, the probability of passage of a proton or a halogen ion through a cell having in its structure six bonds of CHROMIUM-OXYGEN is much less than through a cell having only three bonds of CHROMIUM - OXYGEN. The creation of mechanical obstacles occurs for the passage of halogen ions inside the stainless-steel cell structure. Also, the chemical resistance of the cells will increase significantly, since it is known that the CHROMIUM - OXYGEN bond has great chemical resistance. The possibility of breaking the bond of CHROMIUM -OXYGEN bond by protons and negative halogen ions (fluorine) has been calculated by quantum chemical method of PM3 (Parametric Method 3). This method is specifically designed to take into account the parameters of oxygen and halogens [20, 21]. The calculation showed that protons and negative halogen ions cannot break the bond of CHROMIUM-OXYGEN. The calculation showed that protons and halogen ions are trapped by the chromium atom in physical traps, which is consistent with experimental data on the strong saturation of chromium with hydrogen. It is also known that the surface of pure chromium or oxidized chromium at room temperatures does not interact with aqueous solutions of negative halogen ions, nor does metallic chromium interact with pure water, i.e. with the proton [22], which is formed in any water because of dissociation.

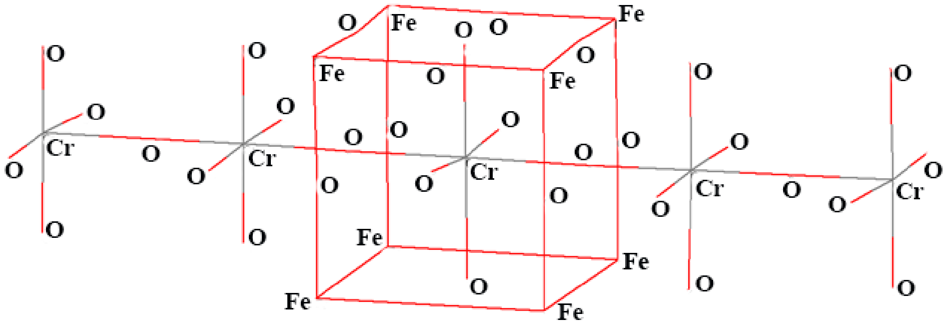


**Fig.3.** Scheme of possible arrangement of chromium and oxygen atoms in the cell structure.
2 layers of stainless steel surface with chromium content from 12 to 18%. Valence of chromium 6.

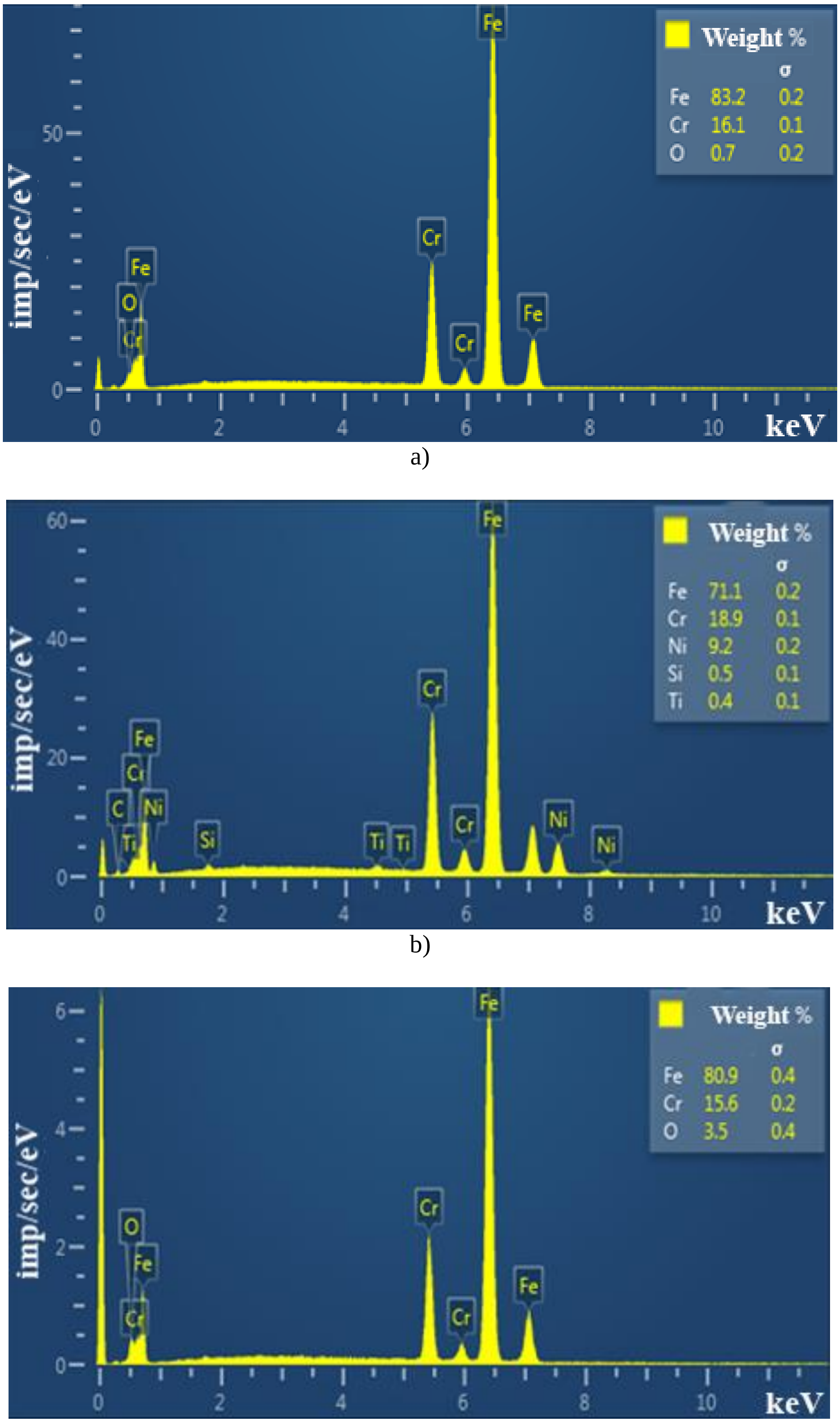
Summarizing the above, it can be stated that the transition of most of the chromium atoms on the surface of stainless martensitic steel from the trivalent state to the hexavalent state due to the formation of three new chromium-oxygen bonds should occur in the presence of active oxygen forms. The formation of additional three new chromium-oxygen bonds in each cell should significantly increase the corrosion resistance in seawater of stainless martensitic steels with chromium content less than 18% (having cubic body-centered lattice).

Experiments were conducted to test the hypothesis that increasing the number of OXYGEN-CHROMIUM bonds in the cells on the surface of stainless martensitic steel will result in a significant increase in corrosion resistance. The purpose of the experiments was to determine the corrosion rate on the surface of X17 stainless martensitic steel with 16% chromium content of 5% in iodine solution in ethanol. Two phenomena should be registered simultaneously when increasing the number of OXYGEN - CHROMIUM bonds. An increase in the percentage of oxygen on the surface of stainless steel and a decrease in the corrosion rate. A sample of untreated X17 steel was placed for 96 hours in an alcoholic iodine solution under normal conditions (T= 0 °C, P= $10^5$ Pa, oxygen concentration 19-21% by volume). The sample was completely immersed in alcoholic iodine solution, with air above it. The lid of the vessel was hermetically sealed.

The percentage composition of the steels is shown in Figures 4, a-c. Micrographs of the X17 steel specimen were taken before placing it in a container of iodine solution (Figure 5, a). The specimen was polished to a shiny condition. Directional roughness is clearly visible for this specimen.

A similar experiment was performed with a sample of the world's most melted carbon steel St3 (A57036) with a chromium content of 0.3% or less. Also, a sample of X19H9T stainless steel was placed in a 5% alcoholic iodine solution for 96 hours (Figure 4, b). We used X19N9T stainless steel as a benchmark of corrosion resistance to compare the investigated stainless-steel samples with insufficient chromium content. The experiment showed that after 96 hours in 5% iodine solution in ethanol, the reference sample of stainless steel X18H9T with high chromium content lost 0.39% of the initial mass (was 0.39924 g, became 0.39770 g).

At the same time, the sample of X17 stainless steel with insufficiently high chromium content and complete absence of nickel lost 1.96% of the initial mass (was 0.57722 g, became 0.56589 g). That is, the corrosion rate is more than 5 times greater in X17 stainless steel with insufficiently high chromium content than in X19H9T stainless steel with more than 18% chromium content and 9% nickel content. The presence of pitting was detected in a micrograph at 400× magnification in a sample of X17 steel after being in a 5% alcoholic iodine solution for 96 hours (Figure 5, b). The average grain size of pitting is 1.1 µm.



a)

b)

c)

**Fig.4.** Energy-dispersive X-ray spectra: a) Percentage content of elements in untreated X17 stainless steel; b) Percentage content of elements in X19N9T stainless steel; c) Component composition of X17 steel after complex 6- hours treatment with air heated to 350 °C and UVT.

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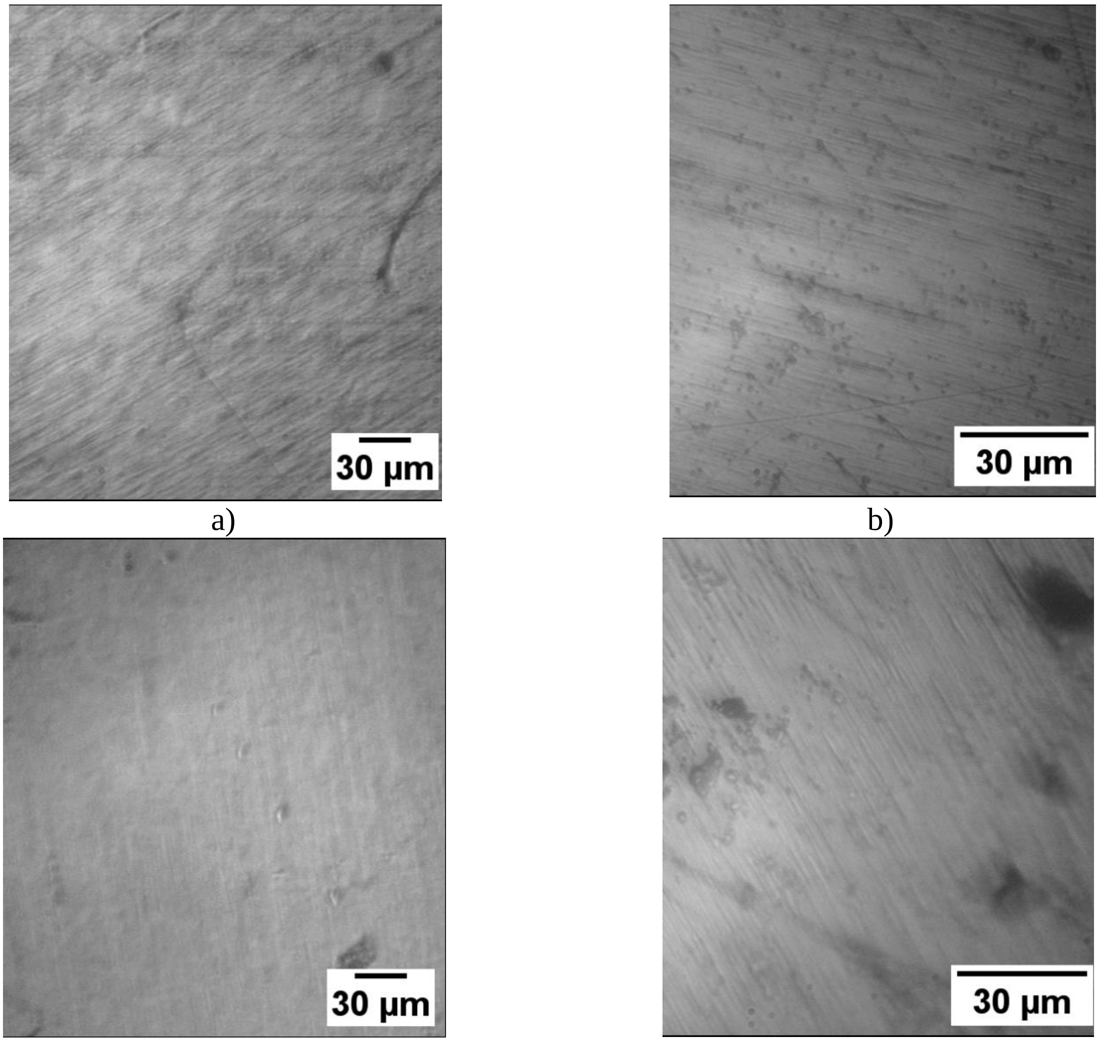
A sample of structural steel St3 (A57036) lost 25% of its weight during 96 hours in a 5% iodine solution in ethanol. St3 contains no less than 98% iron and no more than 0.3% chromium. It was found that even not very high quality X17 stainless steel (which has no nickel and molybdenum in its composition) corrodes in halogen solutions 12 times slower than the most common carbon structural steels. The experiment was conducted to clarify how the interaction of negative halogen ions with the surface of X17 stainless steel leads to corrosion of this steel. The comparative effect of alcoholic iodine solutions on X17 stainless steel samples was studied in the experiment. 5% and 2.5% iodine solutions in ethanol were used. One sample of X17 steel was placed in pure ethyl alcohol. Additionally, one sample was placed in 2.5 % aqueous-alcohol iodine solution. Distilled water and ethyl alcohol were in equal volume doses.



a) b)

c) d)

**Fig.5**. Surface microphotographs of X17 steel samples on HV1000 optical microscope:
a) untreated steel at 160x magnification (directional roughness is clearly visible); b) 400x magnification of the steel surface after 96 hours in 5% alcoholic iodine solution (pitting is clearly visible); c) sample at 160x magnification after 6 hours UVT treatment at 350 °C; d) at 400x magnification after 96 hours in iodine solution (sample was previously subjected to 24 hours with UVT at 350 °C.

The experiment showed that corrosion of stainless steel is completely absent for the X17 steel sample after placement in pure ethyl alcohol. It was also found that the corrosion rate was 4.7 times higher than that in 2.5% iodine alcohol solution and 8.4 times higher than that in 2.5% iodine water- alcohol solution after being 96 hours in 5% iodine alcohol solution. These results revealed a clear dependence of the corrosion rate of X17 stainless steel on the concentration of halogen ions. The higher the concentration of halogen ions is the higher the corrosion rate. It was also found that protons slow down the corrosion process of stainless martensitic steel. Protons always formed in water by dissociation [19]. It is very likely that protons in seawater reduce the corrosion rate due to electrostatic interaction with negative halogen ions.

Samples of X17 steel were exposed to high-energy forms of oxygen in order to create on the surface of this stainless steel a monolithic oxide layer in which all chromium atoms are in the hexavalent state. Ozone $O_3$ and singlet oxygen $^1O_2$ are significantly more chemically active than molecular oxygen $^3O_2$ in the ground triplet state [23]. The high-energy molecules of singlet oxygen $^1O_2$ and ozone $O_3$ were assumed to additionally activate the three valences of chromium atoms. Chromium atoms have six valence orbital's at 3d5 4s1 energy levels. Chromium atoms are normally trivalent in the normal state, but with three more valence orbital's they are capable of making three more chemical bonds.

Thus, an oxide layer of light brown colour was formed on the samples of treated X17 stainless steel as a result of 6 hours exposure. The oxide layer at 12 hours treatment was much darker. At the same time, no increase in the mass of the samples was recorded. It indicated that the oxide layer is very thin. The oxide layer has sufficient mechanical strength. Component composition analysis showed 400% increase in the oxygen content on the surface of the sample subjected to 6 hours treatment (Figure 4, c). The oxygen content on the surface of the X17 stainless steel sample treated for 6 hours increased 5 times from 0.7% to 3.5% (Figure 4, a and c). It was visually determined that as a result of exposure to high-energy forms of oxygen, the surface roughness disappeared (Figure 5, a). The steel surface became almost homogeneous (Figure 5, c).

Further, the treated samples of X17 steel (6 and 12 hours of treatment) were placed for 96 hours in 5% iodine solution in ethanol. This solution simulating the effect of sea water is a very aggressive environment capable of completely dissolving aluminium foil within 24 hours, according to the article [11]. The sample subjected to 6 hours pretreatment with reactive oxygen species lost 1.36 % of mass in 96 hours (was 0.50902 g, became 0.50206 g, mass loss 0.007 g). As a result, the oxide film on the surface of the sample has largely dissolved, discoloured, but still retains some structure and covers 30% of the sample surface. The experiment showed that 6 hours treatment of the surface of X17 steel with reactive oxygen species significantly improved the corrosion resistance of the surface of X17 steel. The mass loss due to corrosion decreased by 30% from 1.96% from the untreated surface of X17 steel to 1.36% from the 6 hours treated surface.

The sample of X17 steel subjected to 12 hours pretreatment for 96 hours of being in 5% iodine solution lost 0.57% of mass. This is comparable to the mass loss of high-alloy steel X19H9T (0.4%). Oxide on the surface of X17 steel covers 80% of the sample after being in 5% iodine solution in ethanol for 96 hours. At the same time, the oxide also discoloured to a light golden shade, as on the sample subjected to a preliminary 6-hours treatment. The oxide is firmly bonded to the surface. The oxygen content on the sample surface at the 12 hours treatment of the samples with reactive oxygen species was 4 %.

X17 stainless steel samples were treated at 350 °C with reactive oxygen species for 24 hours in order to further increase the corrosion resistance. As a result, an even darker colour was formed on the surface of the X17 samples oxide layer (dark brown). These samples practically did not change colour after 96 hours in 5 % alcoholic iodine solution, but deep chips were formed on all samples on the surface covered with oxides during repeated experiments. Holes passing through the oxide layer and partially entering the structure of the stainless steel itself were observed. The occurrence of spalling on the surface is attributed to the high stresses in the oxide layer. Chipping occurs because the volume of fully oxidized stainless steel cells (in which each chromium atom is bonded to 6 oxygen atoms) is much greater than the volume of stainless steel cells in which all chromium atoms are in the trivalent state. The Peeling-Bedworth factor for $Cr_2O_3$ coatings is 2.02 for trivalent chromium. The Peeling-Bedworth factor will be 2.56 for hexavalent chromium. It is known if the factor is greater than 2.5 cracks are always formed.

Analyses of the surface of X17 steel treated with reactive oxygen species for 24 hours showed that the oxygen content on the surface of the samples increased to 5 %. Microphotograph showed the absence of pitting corrosion on the surface outside the spalling (Figure 5, d). A monolithic oxide layer with increased chromium valence is formed on the surface of X17 stainless steel during prolonged treatment with active forms of oxygen. Local damages (spalling) occur due to internal stresses associated with the increase of the cell volume in this layer. The absence of pitting corrosion outside the chipping shows that the halogen solution does not have a chemical effect on the formed monolithic oxide layer of chromium with increased valence.

Analysis of the experiments showed that due to the formation of spalling it makes no sense to subject the surface of X17 steel to a long treatment, at which the mass fraction of oxygen on the surface reaches 5% (24 hours of treatment with active forms of oxygen). It is better to limit the surface treatment to a treatment in which the oxygen level on the surface does not exceed 4 %. Spalling does not occur with 12 hours treatment and the corrosion rate in seawater is 71% lower.

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## 4. Discussion of results

It is revealed that the increase in corrosion resistance of X17 steel occurs with an increase in the oxygen content in the composition of cells on the surface of products from this martensitic steel. The increase in corrosion resistance of X17 steel may be a consequence of the formation on the surface of additional bonds such as CHROMIUM - OXYGENE - CHROMIUM, which do not chemically interact with halogen ions. Additional experiments showed the complete absence of chemical interaction of the fully oxidized surface of pure chromium with 5 % alcoholic iodine solution. An iridescent film of chromium oxide was formed on the surface of pure chromium as a result of 12 hours treatment with reactive oxygen species. The analysis of the composition of the investigated untreated X17 steel showed that there are only two main components in this steel iron atoms and chromium atoms with a small amount of oxygen (0.7% mass fraction of oxygen in X17 steel, with all oxygen in the surface layer 4 nm thick [4]). The mass fraction of oxygen on the surface increased to 4% at 12 hours treatment with active forms of oxygen. There was an increase in the oxygen content of 5.7 times. The corrosion rate of X17 steel at the same time decreased by 71%. All oxygen in this case is in the form of oxygen bridges either between chromium atoms or between iron atoms. Experiments conducted with oxidized surface of St3 steel showed an increase in the corrosion rate of St3 steel samples with oxidized surface compared to samples of unoxidized St3 steel by 2.2% when placed in a 5% alcoholic iodine solution. The whole surface of the steel samples was covered with $Fe(OH)_3$ rust. Therefore, the increase in the number of IRON-OXYGEN-IRON type bonds on the surface comes to increase the corrosion rate of steel St3. Summarizing the above it is possible to allocate two important facts:

1) Increasing the number of IRON-OXYGEN-IRON bonds accelerates the corrosion process of products;
2) Increasing the number of CHROMIUM - OXYGEN - CHROMIUM bonds reduce the corrosion rate of products.

5.7 increases in the number of oxygen bonds with a simultaneous increase in corrosion resistance by 71 % in X17 steel occurred as a result of 12 hours treatment with active forms of oxygen. Considering this, it can be concluded that most of the oxygen introduced into the surface of X17 steel formed CHROMIUM - IRON - CHROMIUM bonds. Table 1 shows the data of the experiments performed.

**Table 1.** Dependence of mass loss on steel grade and surface treatment of specimens.

| | St3, Untreated | St3, UVT, 350 °C, 12 hours | X17 Untreated | X17, UVT, 350 °C, 6 hours | X17, UVT, 350 °C, 12 hours | X19H9T | Chromium (99.99 %) | Chromium (99.99%) coated with chromium oxide |
|---|---|---|---|---|---|---|---|---|
| Sample weight loss over 96 hours | 25% | 27.2% | 1.96% | 1.36% | 0.57% | 0.39% | 0% | 0% |

Dependence of mass loss is shown for samples of structural steel St3, steel St3 with strongly oxidized surface, X17 stainless steel without treatment, samples of X17 steel with surface subjected to 6 hours and 12 hours treatment with reactive oxygen species, X19H9T stainless steel, samples of pure chromium, and pure chromium with pre-oxidized surface. These samples were placed in 5% iodine solution in ethanol for 96 hours.

## 5. Conclusions

The following conclusions were made from the results of the studies conducted:

1) It has been shown experimentally that one of the most probable causes of failure of products from martensitic stainless steels with chromium content below 18% in seawater is the interaction of negative halogen ions with the surface of products from these steels. It was revealed experimentally that with increasing concentration of halogen ions in solutions in which steel samples were placed. The corrosion rate of stainless steel increases significantly. The corrosion rate increases 4.7 times in alcoholic solutions when the concentration of halogen ions increases from 2.5% to 5%. In aqueous-alcoholic solutions, the corrosion

rate increases 8.4 times when the concentration of iodine is increased from 2.5% to 5%.

2) It was shown that in seawater corrosion of martensitic steel products with chromium content less than 18% becomes possible due to incomplete oxidation of chromium atoms on the surface of products. It was shown that the rate of corrosion in seawater X17 stainless steel (chromium content less than 18%, completely absent in the structure of nickel and molybdenum) can be significantly reduced (by 71%), after additional oxidation of chromium atoms included in the structure of stainless steel cells. The total oxygen content on the martensitic steel surface increased from 0.7% to 4%. It is revealed that it is optimal to create an oxide layer on the surface of X17 stainless steel with oxygen concentration not more than 4%.

3) The research method used in this article allows reducing costs associated with increasing the corrosion resistance of martensitic stainless steels. This method can be used to increase the corrosion resistance of non-ferrous metals.

**Conflict of interest statement**

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

**CRediT author statement**:

Baikenov M.I.: investigation, formal analysis; Seldyugaev O.B.: conceptualization, writing - review & editing; Guchenko S.A.: investigation, writing - original draft; Afanasyev D.A.: visualization, writing - review & editing.
The final manuscript was read and approved by all authors.

**Acknowledgments**

The authors are grateful to Zinoviev L.A. for discussion of the research methodology used in this article.

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## AUTHORS' INFORMATION

**Baikenov, M.I. –** Doctor of Chem. sciences, Professor, E.A. Buketov Karaganda University, Karaganda, Kazakhstan; ORCID ID: 0000-0002-8703-0397; Murzabek_b@mail.ru

**Seldyugaev, O.B. –** Candidate of Chem. sciences, junior researcher, E.A. Buketov Karaganda University, Karaganda, Kazakhstan; ORCID ID: 0009-0004-9729-1015; oleg.seldyugaev@gmail.com

**Guchenko, S.A. –** Master (Sci.), Junior researcher, E.A. Buketov Karaganda University, Karaganda, ORCID ID: 0000-0002-9954-5478; guchen@mail.ru

**Afanasyev, D.A. –** PhD, Professor, E.A. Buketov Karaganda University, Karaganda, Kazakhstan; ORCID ID: 0000-0002-0437-5315; a.d.afanasyev2@gmail.com