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Resistance of alloys in seawater

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ABSTRACT

Using the methods of optical metallography and scanning electron microscopy, a systematic study of the features of destruction of structurally and crystallographically textured titanium blanks after low-cycle tests in synthetic seawater containing 3.5 % NaCl was carried out. It is shown that corrosion-resistant structurally and crystallographically isolated regions with a basic orientation of the interface and a width of 20–30 μm , which periodically lay over the entire thickness of the workpiece in increments of 100–170 μm , are responsible for reducing fatigue life. The main types of corrosion of steels in sea water are considered. It is shown that for austenitic steels there is a duality regarding the presence of chlorine in seawater: it reduces the activity of microbiological corrosion but increases the risk of pitting and crevice corrosion.

KEYWORDS

corrosion • seawater • microbiological • pitting • crevice corrosion and corrosion cracking

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Introduction

Currently, the Government of the Russian Federation has focused on the development of the Northern Sea Route. The plan includes over 150 projects, including the construction of marine facilities and terminals for the production, storage and transportation of liquefied natural gas, gas condensate.

In accordance with the above, the issue of selecting essential materials resistant to corrosive wear for the manufacture of both primary and auxiliary equipment, applicable under conditions of simultaneous exposure to seawater, atmosphere, and low-cycle vibrations of the floating vessel's hull, is becoming crucial.

The main types of metal and alloy corrosion in seawater are microbiologically influenced corrosion (MIC), crevice corrosion, pitting corrosion, and stress corrosion cracking. Seawater contains a 3.5 % NaCl solution, where the chloride ion shifts the potential of metal atoms towards a lower electronegativity, thereby increasing the corrosion rate. Chlorine ions are easily adsorbed by oxide films on metal surfaces and displace oxygen (passivator) from them, dissolving the passivating films and forming soluble metal chlorides in the process [1].

Stainless high-chromium steels and titanium- and aluminum-based alloys have high resistance to general corrosion. However, in environments with increased chlorine ion content, such as seawater, they can be susceptible to microbiologically influenced corrosion, pitting corrosion, and stress corrosion cracking.

Corrosion in seawater

The primary component determining the corrosive aggressiveness of seawater is halide ions, whose concentration reaches 30 g/L. Testing in seawater exhibits more localized corrosion development and results in greater depth of damage with lower overall mass losses. Moreover, the aggressiveness of seawater is significantly influenced by the oxygen content, the concentration of which depends on the salinity of the water, flow rate, and depth of immersion, and may vary across a wide range.

Previous studies [2–6] have shown that the degradation of materials, such as austenitic stainless steel AISI 316, follows a cumulative effect primarily determined by environmental parameters. These parameters include temperature, chlorine ion (Cl-) concentration, pH level, and flow velocity [7–10].

In addition to environmental factors, the surface and subsurface structures of the material play a crucial role in the onset of mechanical and corrosive degradation. Below, the main types of corrosion characteristic of marine environments are discussed.

Microbial corrosion

Microbiologically influenced corrosion (MIC) is a type of corrosion caused by bacteria or microorganisms (Fig. 1) [11].

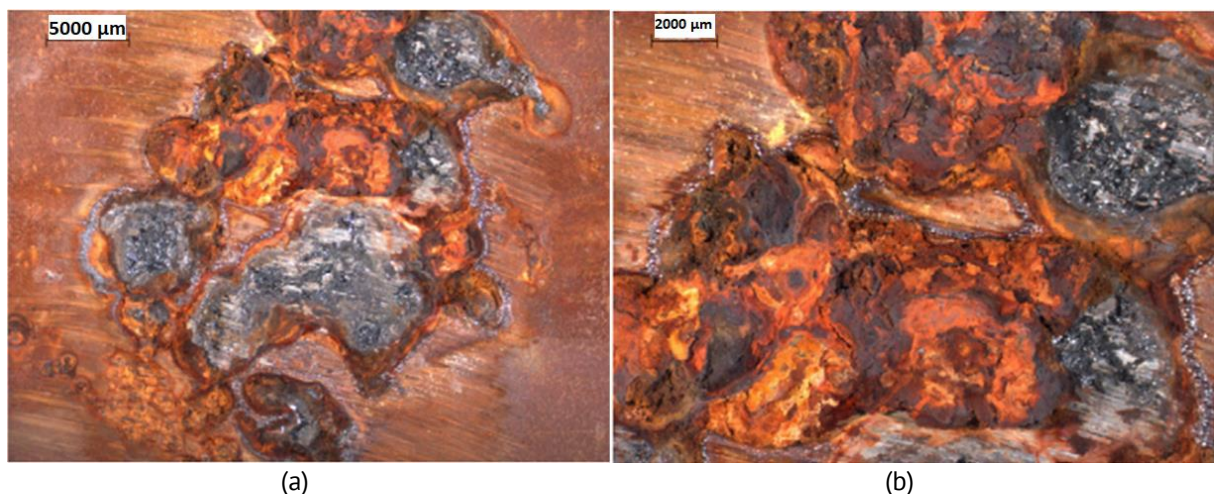


Fig. 1. Corrosion products on the metal surface:
(a) general view ($\times 5$); (b) detailed view of corrosion wear ($\times 10$)

Biological fouling of submerged floating objects results from the development of natural marine biota. Each organism selects ideal conditions for its existence; therefore, the vertical distribution of fouling organisms on both mobile and stationary surfaces is determined by various factors such as light availability, water flow rate, depth, and others. The attachment points of biofoulers are primarily determined by the hydrophilicity and adsorption capacity of the material, and secondarily by the nature and speed of water flow along the surface, as well as micro-turbulence at points where this flow is disrupted [12]. The most studied type of microbiologically influenced corrosion is bacterial corrosion [13].

The term "microbiologically influenced corrosion" does not describe a single corrosion mechanism but rather serves as an umbrella term for various mechanisms

through which microorganisms alter the kinetics of corrosion reactions by their presence or activity. The occurrence of MIC requires the specific interaction of three components: microorganisms, the environment, and the metal. The combination of these components determines different mechanisms that can directly or indirectly change the rate of metal degradation [14].

Pitting corrosion

Pitting corrosion (Fig. 2) is the most destructive form of corrosion, as cavities ("pits") form on local, difficult-to-detect areas of the surface. The causes of the initiation and propagation of pitting corrosion wear are heterogeneous inclusions, local defects in the protective corrosion-resistant film such as cracks, scratches, abrasions, etc.

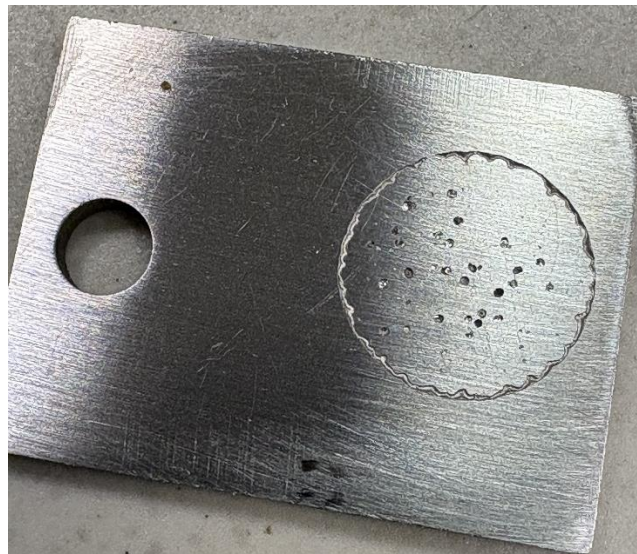


Fig. 2. Pitting and crevice corrosion on the metal surface

The mechanism of pitting corrosion is electrochemical in nature: during its formation, the "pit" becomes the anode, and the base metal becomes the cathode (Fig. 2).

The influences of various factors on corrosion in seawater are complex and, in some cases, contradictory due to their interactions and the dominance of one factor over others. The high salt content in seawater leads to high electrical conductivity, which causes an increase in the rate of corrosion. The impact of seawater salinity on corrosion is maximized when the concentration of NaCl exceeds 10 % [15]. The catalysts (accelerators) of pitting corrosion include: chlorides that contaminate the metal surface and hinder surface passivation; oxygen that accelerates the cathodic reaction; and residual chlorine, which is a strong oxidizer and, when entering the "pitting", locally lowers the pH of the environment within the cavity.

Crevice corrosion

Crevice corrosion is a type of localized corrosion that occurs within "crevices" formed by metal-metal and metal-nonmetal pairs. In terms of the destruction mechanism, crevice

corrosion is identical to pitting destruction. The primary difference lies in the mechanism of the initiation of destruction.

The initiators of destruction are small cavities or "crevices" where localized corrosion occurs [16]. These crevices can be formed due to the geometric characteristics of the structure, such as in the areas of welded, riveted, and threaded joints; the contact of metal with non-metallic solid bodies, such as plastics, rubber, and glass; or the deposition of sand, dirt, or corrosion products on the metal surface.

Such crevices can allow fluid to penetrate, creating a stagnant zone and, at the same time, restricting the access of oxygen from the outside necessary to maintain the integrity of the metal's passive layer. This leads to the weakening of the metal's passive layer, accumulation of dissolved metal ions inside the crevice, and consequently, a decrease in the pH of the environment within the crevice. Subsequently, the destruction process proceeds according to the pitting corrosion scenario.

Especially sensitive to crevice corrosion are certain metals whose passive state on the surface is maintained through the access of oxidizing agents. These metals primarily include stainless steels, aluminum, and titanium alloys, which are crucial structural materials.

Selection of stainless steels and control of service conditions

The main method of preventing corrosion damage is the correct selection of steel grades based on the content of alloying elements. With an increase in the content of chromium, molybdenum, and nitrogen in the steel, its corrosion resistance increases. For instance, steel grades such as 10Cr17Ni3Mo2Ti and 12Cr18Ni12Mo3TiL exhibit high corrosion resistance in seawater.

Another common method of preventive protection against corrosion damage is the control of external and internal operating conditions. Control of external conditions, such as air humidity, and internal ones, such as restricting water exposure, ambient temperature, regulation of the pH level of the environment, concentration of chlorides, and residual chlorine. For example, temperature control allows avoiding critical temperatures for pitting formation; reducing chloride concentration decreases the intensity of the cathodic reaction on the steel surface; control of residual chlorine (chlorines) creates an unfavorable environment for the activity of microorganisms [17]. Inhibitors, when added in small quantities, slow down corrosion and differ in their mechanisms and nature of action [18]: passivating and adsorptive; by the chemical nature of types of media: acidic corrosive, hydrogen sulfide, petroleum, neutral, atmospheric; by the degree of metal surface blockage [19].

Stress corrosion cracking

Steels and alloys are also susceptible to brittle corrosion cracking (SCC) under stress [20,21]. Depending on the material and the aggressiveness of the environment, fractures can be either intergranular or transgranular in nature [22] and may be one of the main causes of product failures [23,24]. Stress corrosion cracking occurs under the influence of constant or cyclic mechanical loads in a corrosive environment (3.5 % NaCl). Stress

corrosion cracking is one of the most unpredictable and dangerous types of destruction, occurring during the operation of high-strength steels and alloys in seawater.

In [25], it was shown that the entire stress corrosion cracking process can be divided in three stages: initiation of crack, propagation of crack and, as the result, fracture.

The process of stress corrosion cracking has the following characteristics: brittle crack propagation in the direction perpendicular to tensile stresses; formation of branching intergranular, transgranular, or mixed cracks; dependency of steel and alloy susceptibility to SCC on relative humidity [26] and the level of externally applied tensile stresses [27,28].

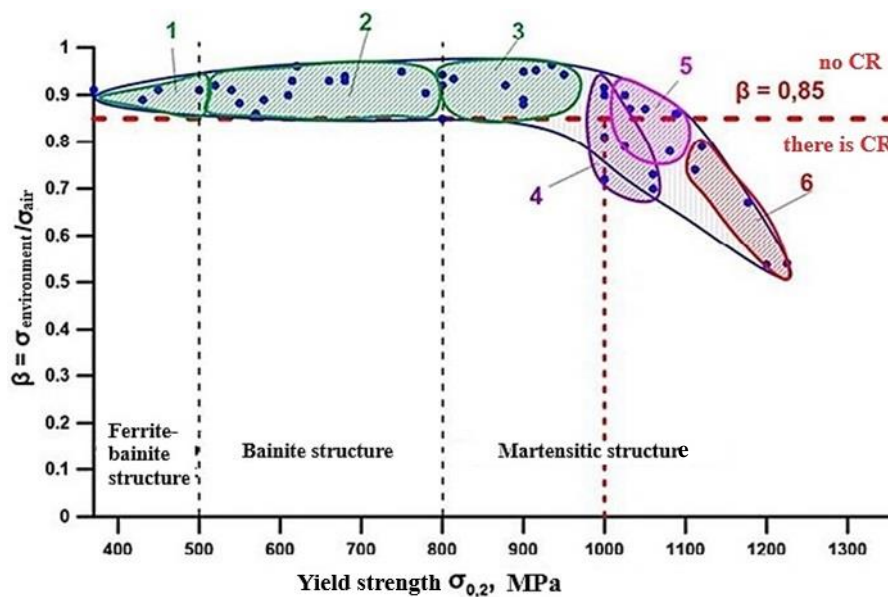


Fig. 3. The dependence of the coefficient of inclination to CR, β , obtained during the 3.5 % NaCl test by the stepwise cantilever bending method, on the yield strength: 1 – ferrite-bainite low-alloy steels; 2 – bainite-martensitic medium-alloy steels; 3 and 6 – martensitic alloy steels; 4 – low carbon martensitic steels; 5 – medium carbon martensitic steels

Figure 3 shows the testing results of high-strength steels with different structural and phase composition obtained on the basis of [29] using the cantilever bending method for SCC in seawater under stepwise increasing loads. It was found that steels with ferrite-bainite, bainite-martensite, and martensite structures and corresponding yield strength values in the range of 370 to 1000 MPa do not show susceptibility (β) to SCC under general corrosion conditions (regions 1–3, Fig. 3). The highest susceptibility to SCC was shown by martensitic low and medium carbon alloy steels with a yield strength of 1200 MPa (region 6, Fig. 3).

Corrosion damage prevention of stainless steels

The primary method for preventing corrosion damage is the rational selection of steel grades based on their chemical composition, where corrosion resistance increases with the content of the alloying element chromium. For instance, grades such as 10Cr17Ni3Mo2Ti and 12Cr18Ni12Mo3TiL, containing 17–18 % Cr, exhibit high corrosion

resistance in seawater. The simplest and most common method for assessing the corrosion resistance of a steel in specific conditions is the pitting resistance equivalent number (PREn). The value of PREn depends on the percentage content of alloying elements in the steel and is calculated by:

$$\text{PREn} = \% \text{Cr} + 3.3 \cdot \% \text{Mo} + 16 \cdot \% \text{N}. \quad (1)$$

It is evident that the main alloying elements that increase corrosion resistance are chromium, molybdenum, and nitrogen. Table 1 presents some of the most widely used steel grades, in order of increasing corrosion resistance. Chemical compositions are taken from [30].

Table 1. Steel grades and PREn

Steel grade	PREn value	Steel type
304	19	Austenitic
316	24	
317	30	
904L	34	
2205	38	Duplex
255	44	Superduplex
2507	48	
6Mo / 254 SMO	46	Superaustenitic

Another common method for preventive protection against corrosion damage is the control of external and internal operating conditions, such as air humidity and exposure control. Internal condition control is conducted, for example, by limiting the influence of water or environmental temperature, regulating the pH level, or controlling chloride and residual chlorine concentrations. For instance, temperature control helps to avoid critical pitting temperature; reducing chloride concentration decreases the intensity of the cathodic reaction on the steel surface; controlling the residual chlorine (chloramines) creates an unfavorable environment for microbial activity. Inhibitors, or corrosion retarders, are substances used to slow down or prevent corrosion when added in small amounts to an aggressive environment.

Corrosion inhibitors vary in their mechanisms and nature: passivating and adsorptive; by chemical nature in different environments: acidic corrosive, hydrogen sulfide, oil, neutral, atmospheric; by the degree of surface blocking of the metal.

However, as evidenced by the aforementioned, these methods cannot be applied indiscriminately because reducing the risk of one type of corrosion might increase the risk of another. For example, in preventing microbiological corrosion by introducing so-called biocides, the activity of microorganisms is significantly reduced or entirely stopped, which in turn leads to a substantial decrease in the overall pH of the environment, hence increasing risks of pitting and crevice corrosion.

In [30], it was found that maximum operational temperatures as well as maximum residual chlorine values for certain cases. For instance, for pipelines, pumps, vessels, and other equipment operating in seawater conditions, the maximum residual chlorine value is 0.7 mg/L. This value is to be considered as a guideline rather than a strict standard requirement.

Materials and Methods

Tests were conducted on low-cycle specimens from the PT-5V titanium alloy with an annular notch, cut from the surface layer of billets so that their axis was parallel to the rolling direction (Fig. 4(a)). Testing was carried out with tension-compression fatigue testing machine in accordance with standard test methods defined in [31]. The colored electrochemical staining was conducted for surface preparation prior fractography inspection.

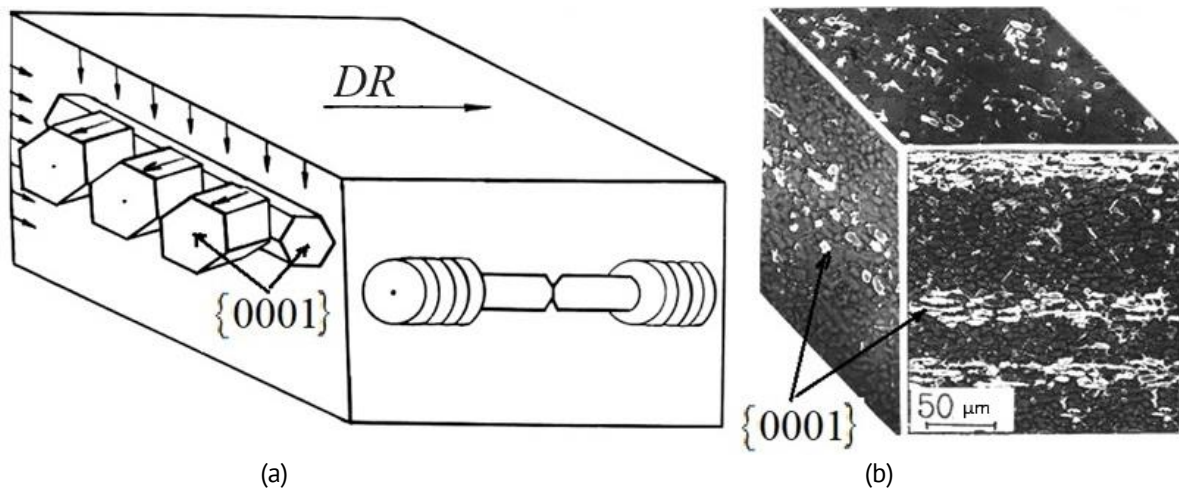


Fig. 4. Sample cutting scheme for low-cycle fatigue tests (a) and structurally-crystallographically isolated areas with the basic orientation of the separation boundaries, revealed by colored electrochemical staining of the workpiece (b)

The structural texture of the studied materials was expressed in the preferential orientation of large-angle grain boundaries of flattened and elongated α -phase particles (Fig. 4(b)). Crystallographic texture was observed in the preferential orientation of the elementary hexagonal cells of the α -titanium crystal lattice (Fig. 4(a)). The texture of the material had a layered structure.

These layers with a basic $\{0001\}$ orientation of structurally and crystallographically distinct regions with a width of 20–30 μm periodically with a step of 100–170 μm were distributed throughout the thickness of the billets. The presence of such regions in the material altered the failure mechanism and increased the scatter in values of low-cycle fatigue resistance in specimens from two-phase titanium alloys.

Results and Discussion

A total of 120 specimens were tested in a 3.5 % NaCl solution in a zero-tension mode with a pulsating loading cycle at a frequency of 2–3 cycles per minute with an applied stress amplitude of 0.8 and 0.7 of the average yield limits (Fig. 5).

The test results showed that at loads of $0.8 \sigma_y$ and $0.7 \sigma_y$, the number of cycles to failure ranged from 200 to 1900 and from 700 to 3800 cycles, respectively. Thus, as the level of applied stress decreased, the scatter in the number of cycles to failure increased.

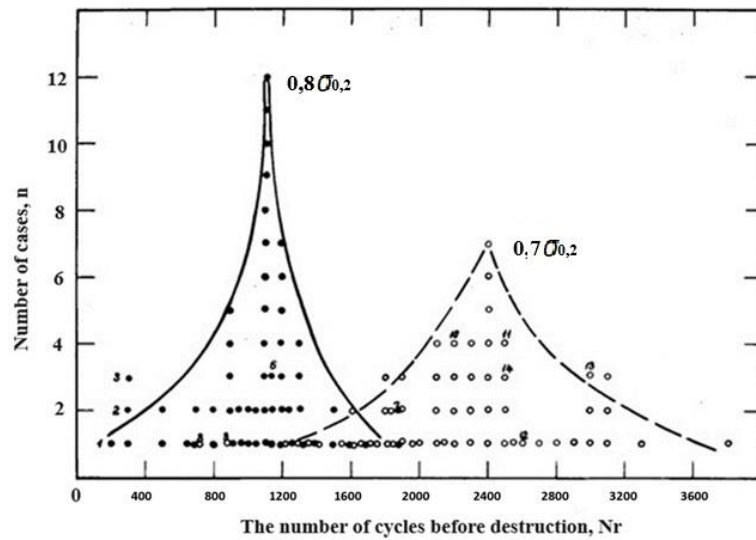


Fig. 5. Results of the low-cycle fatigue tests of the PT-5V alloy

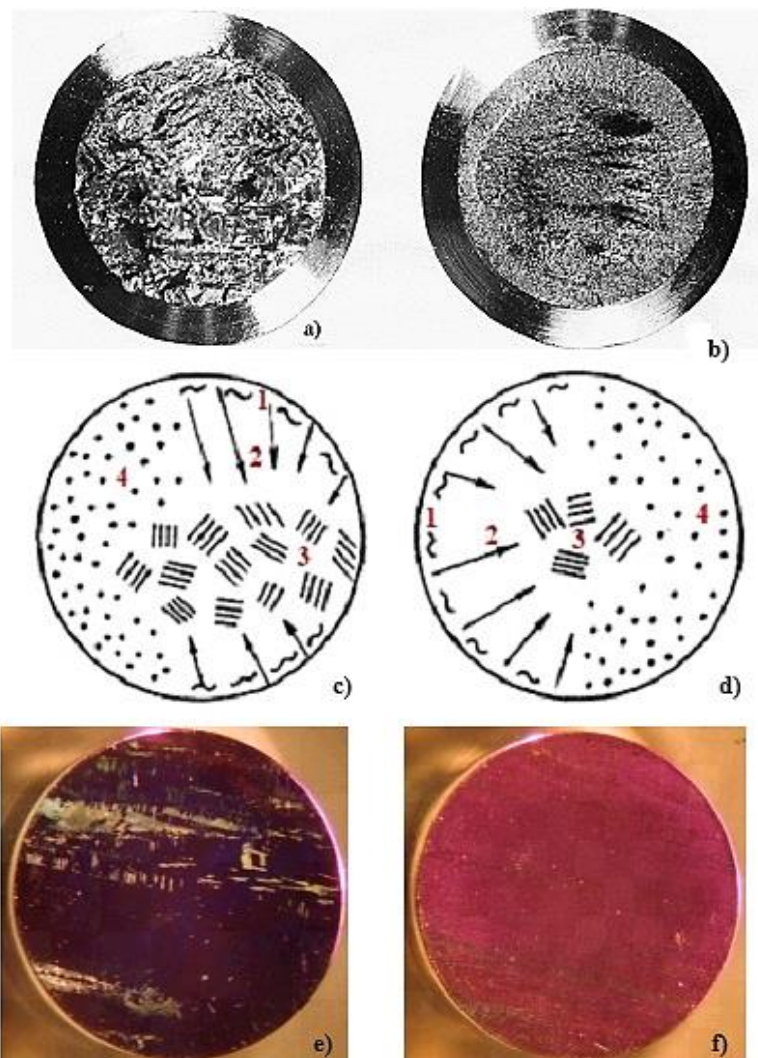


Fig. 6. Characteristic fractures (a,b), destruction schemes (c,d), and structurally-crystallographically isolated areas with the basic orientation of the separation boundaries, revealed by colored electrochemical staining of low-cycle samples (e,f), tested in a 3 % NaCl solution with low ($N = 269$) (a,c,e) and high ($N = 1885$) (b,d,f) numbers of cycles to failure

Fractographic analysis of the macro- and micro-topography of the fractures of the tested specimens (Fig. 6(a,b)) allowed the conclusion that as the main crack length increased and the live cross-section of the specimen decreased, four characteristic fracture zones formed on its surface (Fig. 6(c,d)). The initiation zone of the fatigue crack (zone 1) transitioned into an area of stable crack propagation with large fields of regular fatigue striations (zone 2). The accelerated crack growth area showed a mixed mechanism of fatigue rupture and single-event corrosion cracking (zone 3). Finally, the zone of final failure corresponded to rapid static fracture of the remaining cross-section (zone 4).

The micro-topography of zone 3, representing corrosion cracking, appeared as a mosaic of misoriented fracture facets " $G(10\bar{1}0)$ " (Fig. 7(b)) and perpendicular macro-groove colonies " $K(0001)$ " (Fig. 7(b)). In fractures of specimens tested in air, although macro-grooves were present, corrosion cracking facets were not observed (Fig. 7(b)).

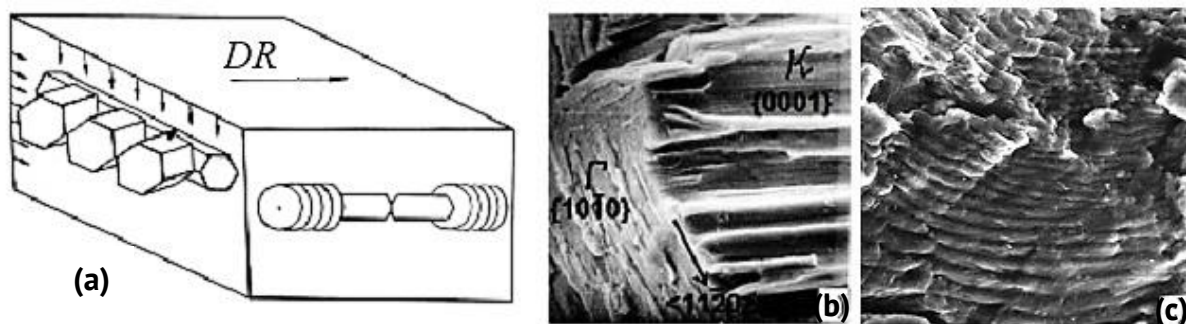


Fig. 7. Destruction scheme (a) and characteristic fracture appearance of low-cycle samples after testing in seawater (b) and in air (c)

In specimens with low cycle counts to failure, the corrosion embrittlement zone occupied most of the surface and reached the edge of the specimen. Color electrochemical staining of the metal directly below the fracture allowed the identification of structurally and crystallographically distinct regions with basic boundary orientations and widths of 20–30 μm , periodically layered with a step of 100–170 μm throughout the billet thickness (Fig. 6(d,e)).

In specimens with high cycle counts to failure, the corrosion cracking zone was either absent or located in the middle of the fracture. Electrochemical staining of these specimens revealed the absence of elongated α -phase particles with basic boundary orientations in the plane of main crack propagation.

Conclusions

In seawater, there is a risk of main types of corrosion: microbiological, crevice, pitting, and stress corrosion cracking. The dual nature of chlorine presence in seawater results in reducing microbial corrosion activity, but increases the risks of pitting, crevice corrosion, and stress corrosion cracking. It was shown that the reduction in low-cycle fatigue endurance is attributed to structurally and crystallographically distinct regions with basic boundary orientations and widths of 20–30 μm , periodically layered with a step of 100–170 μm across the billet thickness. The lower the level of applied stress during cyclic testing, the more significant the crack initiation stage is in the specimen's life time,

emphasizing the importance of considering the quantity and geometry of such structurally and crystallographically distinct regions in flat billets, influencing the macro-mechanism of specimen failure.

References

1. Ajeel SA, Abdul-Hussein BA, Baker YM. Electrochemical measurements of anodizing stainless-steel type AISI 304. *International Journal of Mechanical Engineering and Technology*. 2013;4(3): 63–74.
2. Wyllie WE, Duquette DJ. Effect of dissolved ozone on corrosion behavior of stainless steels in artificial seawater. *Corrosion*. 1998;54(10): 781–799.
3. Malik AU, Ahmad S, Andijani I, Al-Fouzan S. Corrosion behavior of steels in Gulf seawater environment. *Desalination*. 1999;123(2-3): 205–213.
4. Sridhar N, Brossia CS, Dunn DS, Anderko A. Predicting localized corrosion in seawater. *Corrosion*. 2004;60(10): 915–936.
5. Malik AU, Siddiqi NA, Ahmad S, Andijani IN. The Effect of Dominant Alloy Additions on the Corrosion Behavior of Some Conventional and High-Alloy Stainless-Steels in Seawater. *Corros. Sci.* 1995;37(10): 1521–1535.
6. Scatigno GG, Ryan MP, Giuliani F, Wenman MR. The effect of prior cold work on the chloride stress corrosion cracking of 304L austenitic stainless steel under atmospheric conditions. *Mater. Sci. Eng. Struct. Mater. Prop. Microstruct. Process.* 2016;668: 20–29.
7. Nogara J, Sadig J, Zarrouk. Corrosion in geothermal environment: Part 1: Fluids and their impact. *Renewable and Sustainable Energy Reviews*. 2018;82(1): 1333–1346.
8. Kaidrikov RA, Vinogradova SS. Pitting corrosion of metals and multilayer systems (research, modeling, forecasting, monitoring). *Vestn. Kazan. Tekhnol. Univ.* 2010;4: 212–227.
9. Iversen A, Leffler B. Corrosion and Degradation of Engineering Materials. *Corrosion*. 2010;3: 1802–1878.
10. Varchenko EA, Kurs MG. Crevice corrosion of aluminum alloys and stainless steels in seawater. *Proceedings of VIAM*. 2018;7(67): 96–105.
11. Loto CA. Stress corrosion cracking: Characteristics, Mechanisms and Experimental study. *Mor. J. Chem.* 2017;5(4): 622–640
12. Varchenko EA, Kurs MG. Influence of the parameters of the corrosive environment on the properties of structural metal materials during testing in seawater (review). *Proceedings of VIAM*. 2019;9: 85. (In Russian)
13. Kablov EN, Startsev OV, Medvedev IM. Review of foreign experience in corrosion research and corrosion protection products. *Aviation Materials and Technologies*. 2015;2: 76–87.
14. Kaidrikov RA, Vinogradova SS. Pitting corrosion of metals and multilayer systems (research, modeling, forecasting, monitoring). *Technology of chemical production*. 2010;4: 212–227.
15. Ivanova OA, Rodkina AV. The influence of various factors on the corrosion of structural elements of floating structures in seawater. *Vestnik VGAVT*. 2018;56: 50–56. (In Russian)
16. Navid R, Seyed A. Crevice corrosion theory, mechanism and prevention methods. In: *3rd Annual GRASP Symposium. Wichita State University*. 2000. p.215–216.
17. McClements D, Paulsen G. *How to Prevent Pitting Corrosion*. Available from: <https://dz6wltn9e7i51.cloudfront.net/resources/shop-tips/how-to-prevent-pitting-corrosion/> [Accessed 2nd December 2024].
18. Khudyakova LP, Flegentov IA, Kharisov RA, Zhvelev OY, Shestakov AA, Fakhretdinov IR. Investigation of the corrosion resistance of steels to the effects of seawater. In: *Problems of Collection, Preparation and Transport of Oil and Petroleum Products*. 2020. p.89.
19. Kozlova LS, Sibileva SV, Chesnokov DV, Kutuyev AE. Corrosion inhibitors (review). *Aviation Materials and Technologies*. 2015;35: 67–75. (In Russian)
20. Prosek T, Lieberzeit J, Jarvis A, Kiener L. Atmospheric stress corrosion cracking of stainless-steel rock-climbing anchors, part 2: laboratory experiments. *Corrosion*. 2019;75(11): 1371–1382.
21. Frankel GS. Pitting corrosion of metals. a review of the critical factors. *Electrochem. Soc.* 1998;145: 2186–2198.
22. Loto CA. Stress corrosion cracking: Characteristics, Mechanisms and Experimental study. *Int J Adv Manuf Technol*. 2017;93: 3567–3582.
23. Ghosh S, Kain V. Effect of surface machining and cold working on the ambient temperature chloride stress corrosion cracking susceptibility of AISI 304L stainless. *Mater. Sci. Eng. Struct. Mater. Prop. Microstruct. Process.* 2010;527(3): 679–683.

24. Zhang WQ, Fang KW, Hu YJ, Wang SU, Wang XL. Effect of machining-induced surface residual stress on initiation of stress corrosion cracking in 316 austenitic stainless steel. *Corros. Sci.* 2016;108: 173–184.
25. Kharkov AA, Alkhimentko AA, Spaposhnikov NO, Alekseeva EL. SSRT Method: Application to studying the mechanism of stress corrosion cracking in steels and alloys (overview). *Material Physics and Mechanics.* 2021;47(3): 483–492.
26. Katona RM, Taylor JM, McCready TA, Bryan CR, Schaller RF. Towards understanding stress corrosion cracking of austenitic stainless steels exposed to realistic sea salt brines. *Corrosion Science.* 2024;232: 111992.
27. Ren Z, Ernst F. Stress–Corrosion Cracking of AISI 316L Stainless Steel in Seawater Environments: Effect of Surface Machining. *Metals.* 2020;10(10): 1324.
28. International Standard. *BPVC.II.A - BPVC Section II-Materials-Part A-Ferrous Materials Specifications (2 Volumes)*. ASME; 2023.
29. Kostin SK. *Corrosion cracking in seawater of high-strength steels of various structural and phase composition. PhD Thesis.* St. Petersburg; 2018. (In Russian)
30. International Standard. ISO 21452. *Petroleum, petrochemical and natural gas industries – Materials selection and corrosion control for oil and gas production systems.* International Organization for Standardization; 2010.
31. International Standard. ASTM E606/E606M. *Standard Test Method for Strain-Controlled Fatigue Testing.* ASTM International; 2021.

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