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МАТЕРИАЛЫ И ПРОТИВОКОРРОЗИОННЫЕ РАЗРАБОТКИ В МОРСКОЙ И ПОДВОДНОЙ ДОБЫЧЕ НЕФТИ И ГАЗА

М.И. Сизяков

Михаил Игоревич Сизяков (ORCID 0000-0001-6065-6392), ООО «Луховицкая нефтебаза», ул. Советская, 36-А, Луховицы, Московская обл., Российская Федерация, 140501
Область научных интересов: проектирование, обслуживание и эксплуатация газонефтепроводов и газонефтехранилищ.

Mikhail I. Sizyakov (ORCID 0000-0001-6065-6392), LLC "Lukhovitskaya oil depot", Sovetskaya st., 36-A, Lukhovitsy, Moscow reg., 140501, Russia
Research interests: design, maintenance and operation of gas and oil pipelines and gas and oil storages.
E-mail: mixsiz@spbu.su

Освоение углеводородных ресурсов континентального шельфа Российской Федерации и особенно его арктической части и Дальнего Востока, является крупнейшим инфраструктурным проектом, основанным на уникальных разведанных запасах нефти и газа. Континентальный шельф России является крупным национальным запасом углеводородов, который может обеспечить до 25% российской нефти и до 30% российского газа. Наиболее сложные запасы представляют собой сложные условия разработки – высокое давление и низкие температуры, могут находиться в глубоководных или арктических регионах. Современная добыча нефти осуществляется, зачастую, в экстремальных условиях: при высоких давлениях, в агрессивных морских средах и при низких температурах. Комплексный метод разработки месторождений позволяет длительное время поддерживать высокий уровень добычи углеводородов, снижая затраты за счет оптимизации используемых ресурсов и использования общей инфраструктуры. В перспективе наличие производственных мощностей и сервисных баз вблизи арктического шельфа позволит решать мультидисциплинарные задачи, затрагивающие различные сегменты и направления, такие как инженерно-технологический, природоохранный и другие. В данной статье рассматриваются факторы, влияющие на стойкость нефтегазопроводов к коррозии в морской среде. Приведен обзор методов упрочнения и легирования коррозионностойких сплавов для эксплуатации в морской и подводной среде при расширении границ применения традиционных технических сплавов. Проанализированы направления дальнейшего изучения механизмов коррозии и распространения трещин, которые могут привести к разрушению трубопроводов. Исследование наномасштабной коррозии, проанализированное в этой статье, может оказать глубокое влияние на характеристики деградации материалов, применимых ко всей отрасли.

Ключевые слова: морские трубопроводы, коррозия, защита от коррозии, коррозионностойкие сплавы

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MATERIALS AND ANTICORROSION DEVELOPMENTS IN OFFSHORE AND SUBSEA OIL AND GAS PRODUCTION

M.I. Sizyakov

The development of hydrocarbon resources of the continental shelf of the Russian Federation and especially its Arctic part and the Far East is the largest infrastructure project based on unique proven oil and gas reserves. The continental shelf of Russia is a large national hydrocarbon reserve, which can provide up to 25% of Russian oil and up to 30% of Russian gas. The most difficult reserves represent difficult development conditions - high pressure and low temperatures, may be in deep water or arctic regions. As oil resources become more and more heterogeneous, an expansion of various methods of extraction and processing is required, including in extreme conditions, at high pressures in aggressive marine environments and low temperatures. An integrated field development method allows maintaining a high level of hydrocarbon production for a long time, reducing costs by optimizing the resources used and using a common infrastructure. In the long term, the presence of production facilities and service bases near the Arctic shelf will allow solving multidisciplinary tasks that affect various segments and areas, such as engineering and technology, environmental protection, and others. The review article discusses the factors affecting the resistance of oil and gas pipelines to corrosion in the marine environment, the issues of hardening and alloying corrosion-resistant alloys for use in the marine and underwater environment while expanding the boundaries of the use of traditional technical alloys, as well as further study of the mechanisms of corrosion and crack propagation, which can lead to equipment failure and destruction. The study of nanoscale corrosion analyzed in this article can have a profound impact on the degradation characteristics of materials applicable to the entire industry.

Key words: offshore pipelines, corrosion, corrosion protection, corrosion-resistant alloys

INTRODUCTION

Due to the depletion of reserves of traditional oil and gas fields over the past four decades, the industry has moved to the development of more complex fields [1-5] in condition of high pressure and low temperatures in Arctic regions [6, 7].

Thus, the uninterrupted oil production has been carried out on the Russian Arctic shelf for more than 5 years. The continental shelf of Russia is a large national hydrocarbon reserve, which can provide up to 25% of Russian oil and up to 30% of Russian gas [8]. According to the refined results of a quantitative assessment of hydrocarbon (HC) resources, it has been established that reserves of natural gas, condensate, oil and dissolved gas in the amount of more than 122 billion tons of fuel equivalent are concentrated on the shelves of the seas of Russia [9].

Such projects include, for example, Prirazlomnaya and Sakhalin-1. Prirazlomnaya is the first and only Russian project on the Arctic shelf, providing a full production cycle (drilling, production, processing, storage, offloading to tankers). At the peak, it is planned to produce 4.8 million tons of oil equivalent per year in 2022 [9, 10]. Sakhalin-1 is another large project in Russia for the development of hydrocarbon reserves in subarctic conditions; the balanced revenues to the budget of the Russian Federation amount more than 1.2 trillion rubles [11].

In 2014-2020 various sectoral sanctions were introduced, limiting foreign financing of leading state-owned banks, oil and gas companies and Russian oil and gas limited liability companies, access to advanced production technologies [12].

The government introduced an import substitution policy to localize the production of materials and stimulate the development of innovative technologies for the oil and gas sector in order to reduce dependence on imported technologies, as well as to attract foreign investment for the development of high-strength materials, including carbonaceous, as well as corrosion-resistant alloys associated with the production of hydrocarbons in arctic regions. Therefore, great interest has arisen in the study of corrosion-resistant alloys.

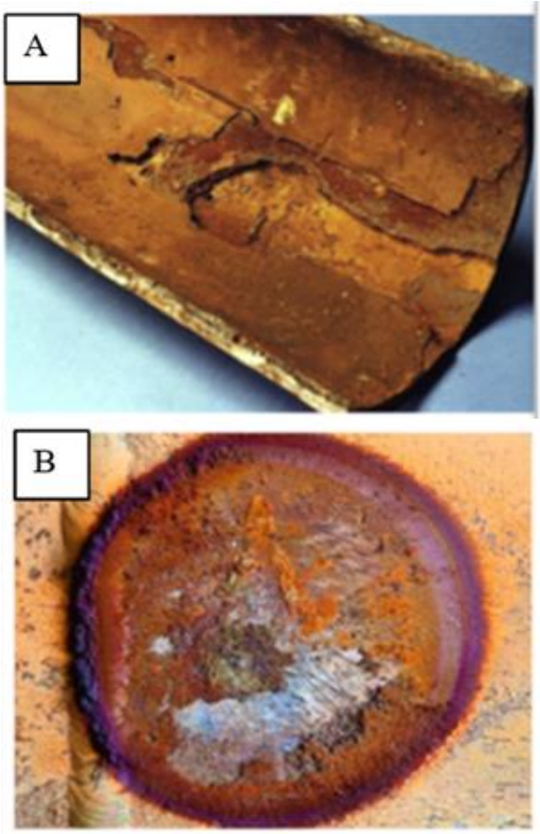

Fig. 1. Common forms of corrosion in transmission oil and gas pipelines: A) internal corrosion, B) pitting [18]
Рис. 1. Распространенные формы коррозии на трансмиссионных нефте- и газопроводах: А) внутренняя коррозия, В) точечная коррозия [18]

There are many review articles on this topic, one of the latest, published in 2020, on the patterns of internal corrosion and anti-corrosion protection of offshore facilities [13]. This review is devoted to environmental cracking of high-strength alloys, methods of hardening and alloying of corrosion-resistant alloys, advanced methods of studying corrosion, such as studying micro- and nanocracks at grain boundaries.

Materials used in oil and gas production in the Arctic regions are exposed to the most aggressive environments. Although the number of serious incidents in the oil and gas industry is not alarming, corrosion of materials can lead to costly catastrophic failures with serious consequences for human life and the environment [14, 15].

This review article discusses the major materials science challenges faced in the oil and gas industry and demonstrates the importance of industry and research synergies.

PREVALENT FORMS OF PIPELINE CORROSION

The Russian Federation as an energy power has an important competitive advantage – a developed and constantly expanding network for the delivery of energy resources [16]. The integrity of pipelines transporting and distributing oil, gas, petroleum products, and other substances is seriously threatened due to electrochemical deterioration (so-called corrosion) [17, 18].

Pipeline corrosion is the deterioration of the material of pipes and associated systems due to their interaction with the service environment. Corrosion of the pipeline and the resulting failures, as well as possible repairs and monitoring costs annually cost the global economy billions of dollars [18]. Corrosion affects all buried or submerged oil and gas pipelines, as they are usually made of metal - mostly steel, with the exception of components and assembly lines.

Corrosion of pipelines occurs due to an electrochemical reaction in the presence of an electrolyte in an aqueous medium; this is usually soil water or fractions of the products that they transport (Fig. 1). Electronic transfer is a very important component of the corrosion process. Monitoring and mitigation systems rely on monitoring the voltages and currents associated with the corrosion process [19].

FACTORS AFFECTING THE RESISTANCE OF OIL AND GAS PIPES TO CORROSION IN THE MARINE ENVIRONMENT

Hydrogen sulfide stress corrosion cracking (HSSCC)

Stress corrosion cracking is the growth of cracking in an aggressive environment. It can lead to unexpected, sudden fracture of normally ductile metal alloys subjected to tensile stress, especially at elevated temperatures [20, 21]. Stress corrosion cracking has a high chemical specificity, as some alloys can only undergo it when exposed to small amounts of chemical environments. The chemical environment that causes cracking for a given alloy is often the environment that causes only minor metal corrosion [22, 23]. Consequently, metal parts with severe stress corrosion cracking can appear bright and shiny while filled with microscopic cracks. Stress corrosion cracking progresses rapidly and is more common among alloys than pure metals [24].

The experience of operating various oil and gas equipment has shown that low- and medium-strength steels with a yield point not exceeding 560 MPa have a sufficiently satisfactory resistance to HSSCC. Earlier, abroad in the oil refining industry, steels with yield strength of 280-390 MPa were successfully used for the manufacture of equipment. However, when using high-strength materials with a yield point of at least 740 MPa, the problem of corrosion destruction of equipment in the presence of hydrogen sulfide arose, which was associated with an increase in the depth of drilled wells.

With an increase in the strength of steel, its resistance to hydrogen sulfide stress corrosion cracking sharply decreases [25-27]. Fig. 2 shows the dependence of the threshold stress, at which no cracking of structural and pipe steels occurs, on the yield strength. With increasing hardness, the tendency to HSSCC increases (the time to fracture decreases). The resistance of steels with the same hardness decreases with an increase in the content of hydrogen sulfide in the medium [28, 29].

As the strength of the steel increases, the probability of fracture along the grain boundaries increases. With an increase in the yield point from 725 to 1210 MPa, the nature of the destruction of steels in an atmosphere of hydrogen sulfide at a partial pressure from 0.13 to 0.44 MPa changes from transcrystalline to intercrystalline [30].

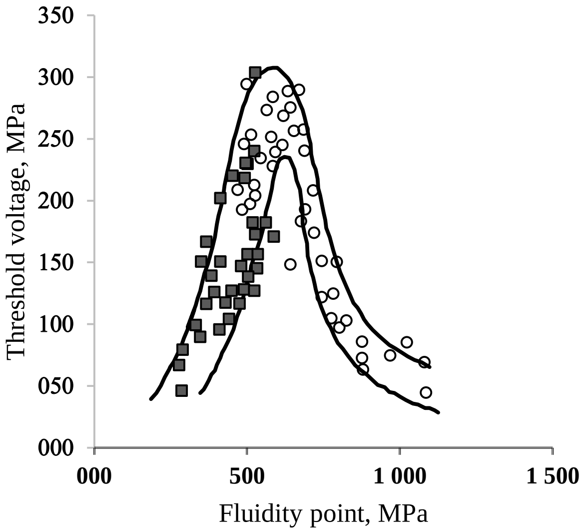

Fig. 2. Resistance to hydrogen sulfide stress corrosion cracking of welded structural manganese (■) and improved pipe (○) steels for oil pipelines, depending on the yield strength [27]. The curves correspond to the boundaries of the scatter of values

Рис. 2. Стойкость к сероводородному коррозионному растрескиванию под напряжением свариваемых конструкционных марганцовистых (■) и улучшенных трубных (○) сталей для нефтепроводов в зависимости от предела текучести [27]. Кривые соответствуют границам разброса значений

Thus, carbon and low-alloy steels with σ0.2 not more than 650 MPa, which corresponds to HRc 22 hardness according to Rockwell, can undergo HSSCC under especially severe conditions. In this case, to increase the resistance to cracking, one should not go to steels with a lower σ0.2, but it is necessary to reduce tensile stresses.

Influence of the chemical composition of steel. Low alloy steels

Steel is a multi-phase material consisting of iron (ferrite) and iron carbide Fe_3C (cementite). Cementite is more chemically stable than ferrite and does not dissolve during carbon dioxide corrosion.

So, the standard nominal composition of typical carbon and low-alloy steels includes, according to the requirements of ASTM A508, from 1.5-2.0 wt.% Chromium (Cr), from 0.4-0.6 wt.% Molybdenum (Mo), from 2.8-3.9 wt% nickel (Ni), carbon (C) content – 0.23 wt%, silicon (Si) – 0.4 wt% [15]. The standard minimum value of the yield strength for such steel is 450-690 MPa.

High strength materials with increased fatigue life are required to overcome the design challenges associated with extreme well pressures and low temperatures in arctic regions. Hydrogen cracking resistance decreases with increasing strength [31]. Thus, there is an upper limit for the safe use of technical alloys in oil and gas production environments, which is arguably more conservative than in other industries [32].

There is no universal definition of what constitutes a high strength material. In the context of this paper, high strength refers to materials with specified minimum tensile strength values above the typical maximum currently recommended for forged carbon and low alloy steels exposed to operating fluids, i.e. 550-586 MPa.

For martensitic and sediment-hardened martensitic foreign stainless-steel grades, such as UNS S41000, UNS S17400, Cr content – 11.5-13 wt%, Ni from 3.0-5.0 wt%, these grades may contain niobium (Nb) – from 0.15 to 0.45 wt%, Carbon (C) – 0.15 wt% [15].

Russian scientists also present their experience in the production of high-strength casing and tubing from corrosion-resistant martensitic steels with a Cr content of 13 wt% [33] with a wide range of strength characteristics, including for achieving minimum yield strengths of 552-758 MPa in pipes in conventional and cold-resistant versions.

Bench and field tests of pipes and developed threaded connections have confirmed the compliance of products with the stated requirements. Based on the test results, the products are used at the facilities of the Gazprom Group.

Exploration and production of oil and gas is moving to the Arctic regions [34]. Components operating in arctic conditions can be exposed to extremely low temperatures, which requires materials and welds that maintain high strength and fatigue characteristics down to -60 °C [35, 36].

Low alloy steels (LAS) are among the most advanced engineering materials. In terms of volume, the use of LAS in various areas of the oil and gas industry far exceeds the use of any other family of alloys [37]. Consequently, improving the properties and productivity of the LAS can have a significant impact on the development of oil fields in difficult conditions.

In spite of their advantages, LASs nevertheless undergo environmental corrosion, for example, in environments containing H_2S, and due to hydrogen generated by cathodic protection systems [38, 39]. The intensity of corrosion of underground metal structures mainly depends on the composition of the soil, its electrical resistivity, the presence of water, oxygen, etc. in the soil [40, 41].

Nowadays, most low carbon steels are accepted for use in H2S environments if they contain 1 wt% Ni and the hardness of the surface exposed to the hydraulic fluid is kept below 250HV. For example, quenched and tempered mild steels with strength values below 550 MPa are believed to withstand exposure to H_2S at stresses up to 100% of their actual yield strength at a total pressure of 1 atm [42].

Data collected by Kappes et al. [43] show that hardened and tempered steels and bainitic steels are the most resistant to sulfide stress cracking. Unhardened steels containing fresh martensite are highly susceptible to hydrogen attack [44, 45].

Researchers have recently developed alloys with yield strengths up to 860 MPa. These materials resist sulfide cracking in mild to moderately acidic operating conditions [46] due to advances in grain boundary development [47-49]. The authors of these works found that the high dissipation energy of special high-angle grain boundaries, more than 30 °, reduces the driving force for crack propagation.

3.3 Hardening and alloying of corrosion resistant alloys for marine and subsea applications

Typically, large diameter subsea field components such as valves, connectors and pipes are made of carbon steel lined with corrosion resistant alloys. In subsea oil and gas production, carbon steel is usually deposited with nickel-containing alloys [50].

Both stainless steel and nickel alloys find numerous applications in the oil and gas industry. In particular, nickel-based alloys are widely used in wellbore components due to their combination of strength and resistance to stress corrosion cracking [51-53]. The most common nickel alloys, for example, UNS N07718 (NA718), contain 17-21 wt% Cr, 2.8-3.3 wt% Mo, 50-55 wt% Ni, Nb, Ta, and Ti [54]. Despite its excellent performance in acidic industrial environments, NA718 is susceptible to pitting and crevice corrosion in oxidizing halogen environments due to the intermediate Cr and Mo content.

There are also other nickel alloys that can withstand the most corrosive acidic environments and are considered to be resistant to seawater [55]. Currently, no standard defines the maximum allowable temperature for seawater service for such alloys; however, according to ISO 21457 the limitation is 30 °C due to crevice corrosion problems in chlorinated systems.

A priori, nickel alloys were considered immune to hydrogen embrittlement under conditions of increased strength [56, 57]. However, during the installation and operation of the equipment, sudden failures and cracks of subsea structural steel components have been reported under relatively favorable conditions associated with hydrogen embrittlement.

A variety of corrosion resistant alloys are used in the oil field, including martensitic, austenitic, ferritic, duplex and stainless steels, annealed and nickel alloys, and titanium, cobalt and aluminum alloys. This number of alloys is required to handle stress corrosion cracking, sulfide cracking, and galvanic induced hydrogen cracking. Standards (ISO, GOST) limit strength and hardness in some alloy systems. The material boundaries established by the standard are derived from a combination of industry experience and qualification testing.

INFLUENCE OF HYDROGEN ON LOCALIZED CORROSION RESISTANCE OF CORROSION-RESISTANT ALLOYS. STUDY OF HYDROGEN-DISLOCATION INTERACTIONS

Hydrogen is the smallest atom in the universe, and the presence of H leads to severe deterioration in strength and toughness. Recent simulations show that the small size of the H atom in the crystal lattice leads to the formation of asymmetric bonds between the H atoms and the host metal [58].

Some authors [59-61] have shown that the hydrogen present in the passive film reduces the resistance to pitting corrosion due to its strong reducing properties.

Thus, a typical, but not trivial, approach is to reduce the sample size and perform micro- and nanoscale mechanical estimates of crack propagation [62, 63].

Undoubtedly, in recent decades, nanoindentation has been the most popular and frequently used small-scale testing method [64].

A typical nanoindentation test consists of several stages. The first one is to obtain an image of the surface relief, then the tip can be positioned with nanometer accuracy. Subsequently, multiple punching of the material can be performed. In such cases, indentation begins with an elastic load that follows the Hertzian contact model [65].

When the shear stress below the tip in the bulk of the material approaches the theoretical stress required for the nucleation of a homogeneous dislocation, a sudden jump occurs. Then indentation continues in elastoplastic mode up to the maximum indentation load. It can be assumed that the unloading curve is completely elastic and is usually used to determine the hardness and elastic modulus of a material by the Oliver-Pharr method [66].

Nanoindentation provides excellent opportunities for studying the effect of hydrogen on mechanical properties, especially the effect of hydrogen on dislocation nucleation. The required load for the nucleation of a homogeneous dislocation decreases in the presence of H; the dislocation nucleates more easily [67].

LOCALIZED CORROSION OF CARBON STEEL AT THE MICRO LEVEL IN REAL TIME

Pitting corrosion in steel is initiated at or near inclusions within the microstructure, such as MnS and iron carbides [68]. However, it is not known why some inclusions, even of the same composition, are more electrochemically active than others [69]. There are three theories explaining this mechanism: (1) orientation of the surface of the iron matrix, (2) galvanic mediation, [69] or (3) disordered and stressed iron matrix [70, 71].

Inclusions of iron carbide, in particular cementite (Fe_3C), are of particular interest in the study of corrosion of carbon steel. Experimental observations of nanoscale solid-liquid interfacial processes are limited by the complexity of reproducing the flowing corrosive medium inside a device capable of characterizing rare, stochastic, and corrosion-initiating events occurring at the nanoscale [72].

Some authors [73] studied steel corrosion processes using TEM methods to obtain a temporary object-specific nanoscale visualization of localized corrosion processes occurring simultaneously on many different solid-liquid interfaces present in a pipeline sample from the real world.

The fully characterized sample was placed in a liquid chamber for real-time observation under water flow. The corroded sample was then characterized using TEM methods.

In one area near the center of the steel specimen, clear signs of localized accelerated corrosion were found. The first signs of localized corrosion were visible after 40 min of exposure to liquid electrolyte, as indicated by the rapid changes in intensity in the TEM micrographs. Comparison of these brighter areas with preliminary structural data showed that the initiation of corrosion occurred in a triple junction formed by an isolated inclusion of cementite grain and two adjacent ferrite grains. The final microstructure is shown in Fig. 3.

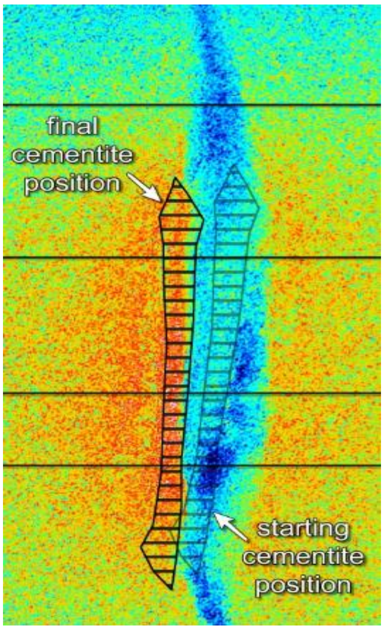

Fig. 3. Inspection of a steel sample where localized corrosion has occurred. Overlay of the original grain boundaries on the TEM image. The contours of the initial (gray) and final (black) place of cementite inclusion are presented [73]

Рис. 3. Обследование стального образца, где произошла локальная коррозия. Наложение исходных границ зерен на изображении ПЭМ. Представлены контуры начального (серого) и конечного (черного) места включения цементита [72]

The imposition of the initial contour of the grain boundary on the final image (Fig. 3) showed that the cementite grain shifted relative to its initial position.

The final photos showed that the ferrite was completely converted to an amorphous corrosion product after 1025 min of exposure. At this point, the ferrite regions of the sample lost about 30 nm, retaining 55 nm as iron oxide. Taking into account the initial thickness of 85 nm and the quantitative scale of the ferrite dissolution time, the rate of loss of corrosive material, due only to uniform corrosion, was calculated in the range from 0.015 to 0.16 mm per year at a penetration depth of 0.044 to 0.44 mm per year. It is expected that these values will be the upper limit, since they were calculated based on the possible contact of both surfaces of the sample with the solution.

Further understanding of the mechanisms of deposition of corrosion products can be achieved through the introduction of new tools and methods that complement TEM in situ and allow tracking the evolution of iron oxide in situ [74].

Nanoscale corrosion pathways like those identified in this article can have a profound impact on the degradation characteristics of materials. This work suggests that different types of electrochemically active processes will create percolation networks that corrode the inner body of steel much more quickly than predicted by uniform corrosion models.

CONCLUSION

High-strength materials, including carbon and low-alloy steels, as well as corrosion-resistant alloys, are necessary to overcome the material obstacles associated with the production of hydrocarbons from unconventional formations under high pressure and corrosive environments.

Environmental cracking and localized corrosion are two major forms of degradation that affect alloys and prevent them from operating safely and economically in high pressure, harsh marine environments and arctic fields. A better understanding of metallurgical factors and manufacturing variables that lead to optimal reduction in stress corrosion cracking is of paramount importance.

The authors declare the absence a conflict of interest warranting disclosure in this article.

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

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