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SUSCEPTIBILITY OF PIPE STEEL OF A CONTROLLABLE ROLLING TO STRESS-CORROSION CRACKING

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Досліджено схильність трубної сталі X70 до корозійного розтріскування від напруження (КРН) в умовах комплексного впливу чинників. Чутливість до КРН оцінювали за коефіцієнтом K_s (співвідношення відносного звуження зразка у повітрі до його відносного звуження у розчині). Сприйнятливості сталі X70 до КРН при потенціалі корозії – низька, але збільшується за наявності концентратора напружень та при застосуванні катодної поляризації. Встановлено деякі відмінності у сприйнятливості до КРН при потенціалі – 1,0 В (відносно хлорсрібного електроду порівняння) трубної сталі X70 різної технології виробництва. При однаковій комбінації чинників найбільший вплив на чутливість до КРН обумовлює наявність концентратора напружень

Ключові слова: *трубна сталь, поляризація, деформація з повільною швидкістю, катодний захист, корозійне розтріскування від напруження*

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1. Introduction

Underground pipelines ensure an efficient and safe way of oil and gas transportation at long distances. Gas oil pipelines is a heterogeneous system, in which during contact with a corrosive and aggressive environment, the of local corrosion processes is thermodynamically probable. In the presence of mechanical stresses, the number types of probable fractures are expanding. One of the most dangerous and difficult-to-predict types of fractures in the main pipelines, which directly deteriorates the reliability of operation of the gas transport system (GTS), is stress-corrosion cracking (SCC) [1, 2]. Therefore, the study of this phenomenon, which is resulting in accidents, has an important scientific and practical significance.

2. Literature review

Depending on the properties of the medium, two types of SCC are distinguished: at high pH [3, 4] and near-neutral pH [5, 6]. Researchers proved that at high pH SCC proceeds in an intergranular mechanism [7], and at near-neutral pH its nature is transgranular [8].

SCC propagates at the simultaneous action of three groups of factors [9]: mechanical stress [10, 11], external environment [12] and properties of the metal [13]. The pipes, used in the section of a pipeline, even with the same chemical composition can have a slight difference in their corrosion-mechanical properties. Some of the researchers believe that the SCC development can be stopped by de-

signing and applying special grades of steel. Undoubtedly, this will increase the resistance of pipe steels to SCC, but will not completely solve the problem.

Despite the development and implementation of the methods, which allow to predict the propagation of corrosion, including the stress-corrosion cracking, thus contributing to a decrease in the overall level of accidents in the main pipelines, a share of fractures as a result of SCC propagation continues to be high. Therefore, it was considered expedient to conduct a study of sensitivity of pipe steel to SCC at a complex influence of different factors.

3. The aim and objectives of the study

The conducted researches aimed to determine the susceptibility to SCC of pipeline steel of a controllable rolling in the conditions of complex influence of factors, in the presence of some difference in the technology of pipe manufacturing.

To achieve the stated goal, the following tasks were set and fulfilled:

- to investigate the corrosion-mechanical properties of pipe steel X70 of a controllable rolling of different manufacturers under conditions of complex influence of factors, in particular: the corrosive environment, potential (E_{cor} , -1,0V, -2,0 V), the accumulated of cyclic stresses, the presence of stress concentrator;

- to evaluate the susceptibility to SCC of pipe steel X70 of controllable rolling of different manufactur-

ers under the influence of the combination of stress-corrosion factors in the range of potentials from the corrosion potential to the potential -2.0 V in a medium with near neutral pH.

4. Materials and methods of research

The object of investigations were the specimens of a pipe steel of X70 type of a controllable rolling, made

from the pipes being in operation (for about 40 years), having a diameter of 1420 mm and a wall thickness of 15.7 mm, conventionally named A and B.

The test solution was an NS4 solution + sodium-potassium phosphate buffer solution in the ratio of 9:1. Composition of NS4 is the following (g/l): 0.037 KCl + 0.559 NaHCO₃ + 0.008 CaCl₂ + 0.089 MgSO₄, pH 8.0 [14].

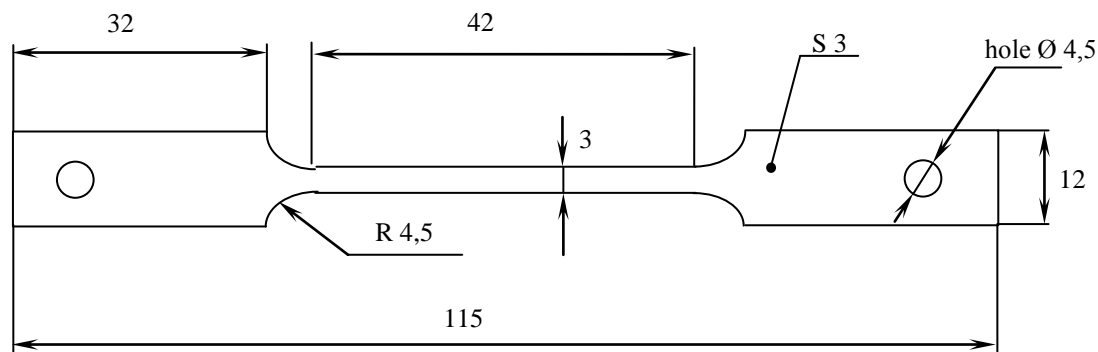


Fig. 1. Sketch of the specimen for testing at a slow strain rate deformation

According to GOST 9.901-1, the method of slow strain rate deformation was applied. Plane specimens, Fig. 1, were subjected to tension in air and in the solution at a rate of 10^{-6} s⁻¹ in the rupture testing machine AIMA -5-1. The cross-sectional area of a test part of the specimens in the initial state was 9 mm². The tests were carried out at a corrosion potential, at the potentials -1.0 V_{Ag/AgCl} and -2.0 V_{Ag/AgCl} (relative to chlorine-silver electrode of comparison). A part of the specimens was subjected to cycling in an elastic region in the range of boundary stresses from 0.4 to $0.8\sigma_{ys}$ (σ_{ys} is yield strength) at a frequency of 10 Hz during 10^5 cycles, the other part of specimens was tested without preliminary cycling (further – specimens in the initial state). To accelerate the initiation of a stress-corrosion crack on the specimen, a local corrosion defect (further LCD) V-shape form with a depth from 0.25 mm to 0.3 mm, mechanically applied on one of the surfaces of the specimen was simulated.

The potential was controlled by potentiostat PI-50-1.1 and the programmer PR-8. The stresses, elongation of the specimen ϵ and test duration were controlled during corrosion-mechanical tests.

5. Experimental results and discussion

5.1. Chemical composition and structure of the pipes

The chemical composition of the metal of the pipes under investigated is shown in Table 1. It is seen that the base metal of the pipe A is a low-carbon steel, microalloyed with vanadium and niobium, which accord-

ing to its chemical composition meets the requirements of TS 14-3-995-81 [15] to the X70 steel category.

The mechanical characteristics of the base metal of pipes under investigation were nearly the same and given below:

- yield strength, σ_{ys} : 498–513 MPa (according to TS 14-3-995-81, not lower than 441 MPa);
- ultimate rupture strength, σ_r : 600–603 MPa (according to TS 14-3-995-81, not lower than 588 MPa);
- relative elongation, ϵ : 21.5–24.2 % (the standard value is not lower than 20 %);
- impact toughness (KCV⁻¹⁵): 224–227 J/cm² (standard value is not lower than 78.4 J/sm²).

In general, the base metal of the pipe under investigated at the standard values of strength, ductility and impact strength (σ_{ys} , σ_r , σ_{ys}/σ_r , δ_5 , KCV⁻¹⁵, KCU⁻⁶⁰) meets the requirements of TS 14-3-995, according to which this pipe was manufactured, and the requirements of SNiP 2.05.06 [16].

The microstructure of the metal in both pipes (Fig. 1) is ferrite-pearlite with a slight structural heterogeneity at different areas of the sheet across its thickness (near the outer surface, as compared to other areas, ferrite grain is somewhat smaller and more elongated along the rolling), which is inherent for the steel of a controllable rolling.

The elongation of ferrite grains in the direction of rolling is very small.

Table 1

Chemical composition of the base metal of the investigated samples of pipes

| Samples' characteristics | Mass fraction of elements, % | | | | | | | | | | | |
|--------------------------|------------------------------|-----------|-------------|-------------|-------------|-------------|------|------|-------|-----------|-------|------|
| | C | Mn | Si | S | P | Al | Ni | Mo | Ti | V | Nb | Cr |
| Pipe A | 0.089–0.101 | 1.33–1.45 | 0.238–0.272 | 0.004–0.005 | 0.012–0.017 | 0.031–0.032 | 0.04 | 0.03 | 0.004 | 0.05–0.06 | 0.027 | 0.04 |
| Pipe B | 0.119 | 1.48 | 0.357 | 0.003 | 0.016 | 0.034 | 0.05 | 0.03 | 0.005 | <0.02 | 0.028 | 0.05 |
| TS 14-3-995-81 | Not more than | | | | | | | | | | | |
| | 0.12 | 1.70 | 0.50 | 0.010 | 0.020 | 0.050 | – | 0.30 | – | 0.08 | 0.06 | – |

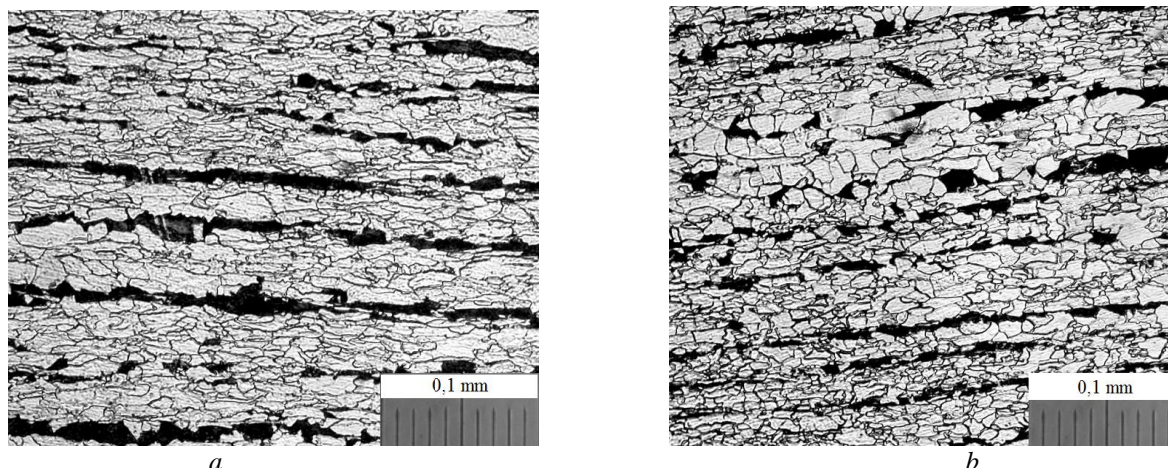


Fig. 1. Microstructure of the base metal of the pipes: a – pipe A; b – pipe B.

Ferrite grain corresponds to 9–10 number for the pipe A and 10-11 number for the pipe B (except for individual grains of 9 number) according to GOST 5639 [17]. According to GOST 5640 [18], banded orientation of the base metal in the pipes A and B was evaluated by the ball 4, row A and by the ball 2, row B, respectively. The amount and dimensions of a perlitic structural component in the metal of the pipe B are slightly smaller than in the metal of the pipe A.

The contamination of non-metallic inclusions in the base metal of both pipes is insignificant, which is typical for the pipe steel of the investigated type. The non-metallic inclusions mainly are line oxides and non-deformable silicates. Almost all of the inclusions are globulized; coarse elongated inclusions are absent. As it is seen from Table 2, the contamination of the non-metallic inclusions in the base metal of pipe A is somewhat higher than in the pipe B.

Table 2

Non-metallic inclusions in the base metal of the pipes samples under investigation

| Sample characteristics | Ball according to GOST 1778 [19] | | | | |
|------------------------|----------------------------------|-------------|-------------|----------------|---------------|
| | oxides | | silicates | | sulfides |
| | spot | line | plastic | non-deformable | |
| Pipe A | 1 (scale a) | 2 (scale b) | 1 (scale b) | 2 (scale b) | 1 (scale a) |
| Pipe B | 1 (scale a) | 1 (scale b) | 0 (scale b) | 1 (scale b) | 0.5 (scale a) |

Therefore, the microstructure of the pipes under investigation is similar, namely ferrite-perlitic, with the exception of slight differences: for the pipe A, a higher contamination of the non-metallic inclusions in base metal, larger ferrite grains and somewhat larger banded orientation are peculiar.

5.2. Slow strain rate tests and the methodical approach to the estimation of SCC susceptibility

During the corrosion-mechanical tests, different combinations of stress-corrosion factors (corrosion-aggressive medium, potential, accumulated cyclic stresses, presence of stress concentrator) were simulated and the sensitivity of the pipe steel to SCC was evaluated under the mentioned conditions.

After rapture of the samples, their cross-sectional area was determined. The degree of sensitivity to SCC was evaluated according to the dimensionless coefficient K_s , which is equal to the ratio of relative reduction coefficient of the sample in air to relative reduction coefficient of the sample in the solution by the formula:

$$K_s = \frac{\psi_n}{\psi_p} \tag{1}$$

$$\psi = \frac{S_0 - S_1}{S_0} \tag{2}$$

where Ψ_n and Ψ_p is the relative reduction coefficient of the samples, respectively, in air and in the solution, S_0 is the cross-section area of the samples before tests, mm^2 ; S_1 is the cross-section area of the samples in the place of fracture after tests in air S_1^n or in the solution S_1^p , mm^2 .

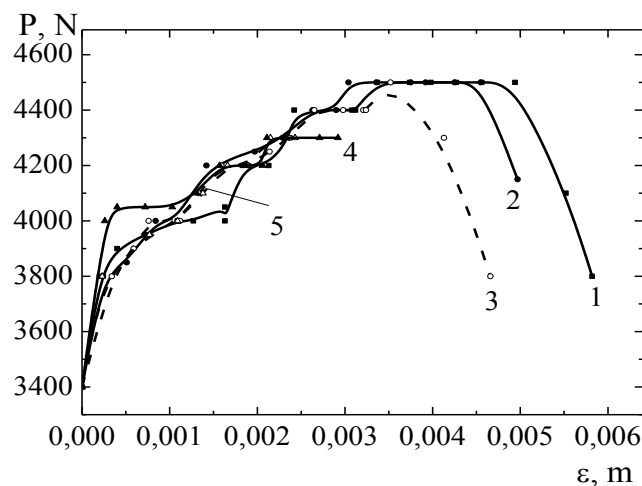
To simulate the effect of cyclic stresses during the long-term operation of the gas pipeline, the samples were preliminary cycled in the range of boundary stresses from 0.4 to $0.8\sigma_t$ at a frequency of 10 Hz during 10^5 cycles.

It is commonly known that a stress-corrosion crack initiates from local stress concentrators, for example, in the form of local corrosion damage (further – LCD). Therefore, to accelerate its initiation in the laboratory conditions, on the samples, V-shaped LCD of ~ 0.2 mm depth was simulated, which was applied to one of the surfaces of the sample by mechanical method. It was assumed that the state of the sample with accumulated stresses and with the simulated LCD could be compared with the state of the MG under operation.

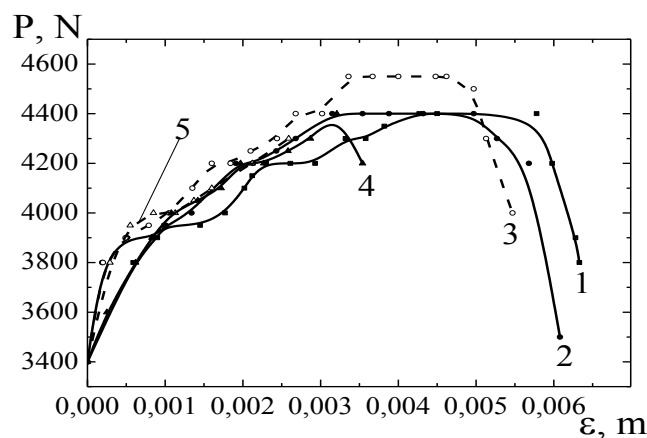
5.2.1. Investigation and estimation of the susceptibility of pipeline steel to SCC at corrosion potential

The curves of mechanical fracture in air and corrosion-mechanical fracture in the solution at the corrosion potential of the samples made from the pipe A are shown in Fig. 2, *a* and from the pipe B – in Fig. 2, *b*.

The fracture of the samples in air was ductile, Fig. 3*a*, 3*b* (photo 1), as is evidenced by the typical neck-down near the place of fracture. For the samples made from the pipe A and B, respectively, the fracture time was ~ 19.5 h and ~ 20 h, the cross-section area was ~ 3.97 mm^2 and ~ 2.91 mm^2 , the relative reduction coefficient was 56 % and 68 %. After the tests in the solution at the corrosion potential, a decrease in the fracture time was observed: for the samples from the pipe A – to ~ 18.3 h and for the samples from the pipe B, the fracture time remained the same. The relative reduction coefficient was decreased to 45 % and 56 %, respectively. Under these conditions, the coefficient of sensitivity to SCC K_S in the metal of both pipes was almost the same – 1.24 and 1.21. Like in air, the character of fracture was ductile (Fig. 3, *a*, *b*, photo 2).



a



b

Fig. 2. Mechanical fracture curves in air and corrosion-mechanical fracture curves of the X70 pipe steel samples made from the pipe A and the pipe B in the NS4 solution under the influence of a complex of stress-corrosion factors at the corrosion potential: *a* – pipe A; *b* – pipe B; 1 – sample in air, 2 – sample in the initial state, 3 – sample after cycling, 4 – sample in the initial state with LCD, 5 – sample after cycling with LCD

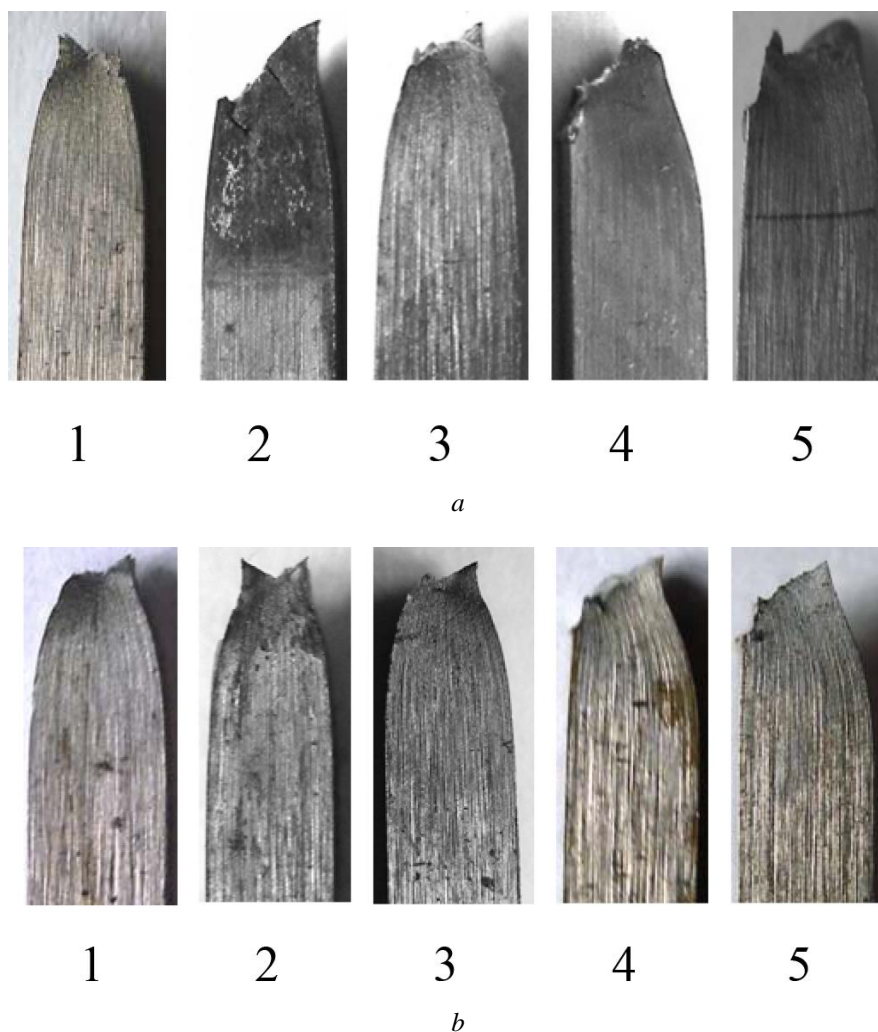


Fig. 3. Photos of fractures of the X70 pipe steel samples made from the pipe A and the pipe B after mechanical tests in air and corrosion-mechanical tests in the solution at the influence of a complex of stress-corrosion factors on the potential of corrosion:

a – pipe A; *b* – pipe B; 1 – sample in air, 2 – sample in the initial state, 3 – sample after cycling, 4 – sample in the initial state with LCD, 5 – sample after cycling with LCD

A preliminary cycling of samples in the elastic region very little changed the corrosion-mechanical properties of the steel compared to the initial state: the fracture time was equal to ~17.0 h and ~19.5 h, the cross-section area was equal ~4.02 mm² and ~3.77 mm², and the coefficient $K_s = 1.02$ for the pipe A and $K_s = 1.17$ for the pipe B. The fracture character of the samples remained ductile (Fig. 3, *a* and 3, *b*, photo 3).

At the presence of stress concentrator, the regularities of the fracture changed significantly: the time of fracture decreased by almost twice: to ~9.5 h for the pipe A and to ~12 h for the pipe B, the cross-section area increased to 5.90 mm² and 4.83 mm². Among the noted changes in the character of fracture (Fig. 3*a* and 3*b*, photo 4), there are a lower plastic deformation of the samples, which correlated with an increase in the degree of sensitivity to SCC: the coefficient K_s was equal 1.65 for the pipe A and 1.48 for the pipe B. The regularities of fracture of the samples after preliminary cycling and in the presence of LCD were as follows: the time of fracture remained almost unchanged as compared to the samples

without preliminary cycling and was, ~10.0 h for the pipe A and ~9.5 h for the pipe B, but the cross-section area somewhat decreased to 4.69 mm² and 3.90 mm², the degree of sensitivity to SCC was: for the pipe A the coefficient $K_s = 1.22$ and for the pipe B – $K_s = 1.19$. The character of fracture was similar to the character of fracture of the same samples without preliminary cycling (Fig. 3 *a*, *b*, photo 5).

At the corrosion potential, the corrosion-mechanical properties of steel made from pipe A and B having slight structural differences, including those after cycling and in the presence of LCD, were almost similar: the fracture was ductile, the sensitivity to SCC was low, the coefficient K_s varied from 1.21 to 1.65 for the samples from the pipe A and from 1.17 to 1.48 for the samples from the pipe B (Fig. 8, *a*).

The sensitivity to SCC at the corrosion potential was most strongly influenced by LCD: in the presence of stress concentrator the decreasing of the fracture time and a part of plastic deformation in the fracture is noted.

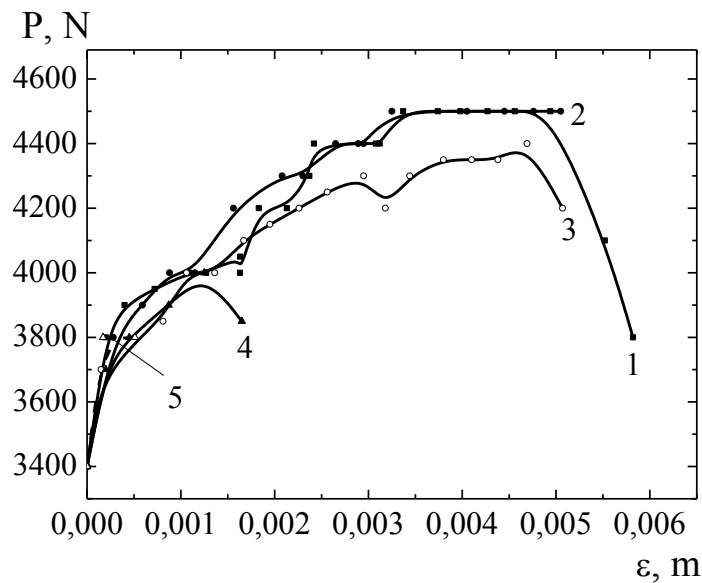
5.2.2 Investigation and estimation of the susceptibility of pipeline steel to SCC at the potential $-1.0 V_{Ag/AgCl}$

The fracture curves are presented in Fig. 4, *a, b*.

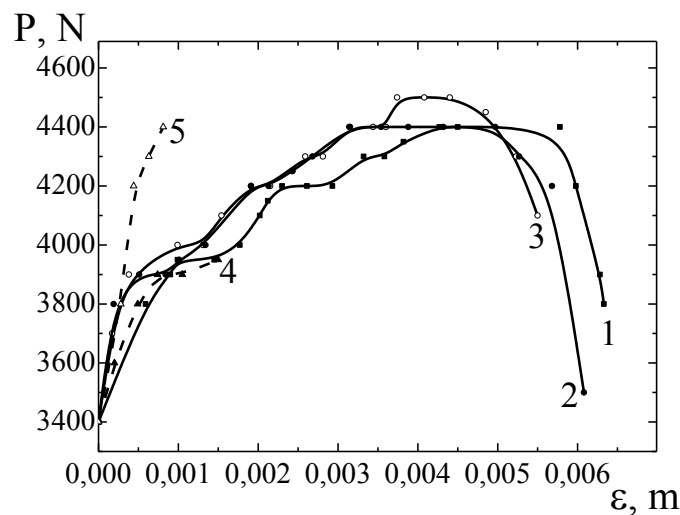
At the potential $-1.0 V_{Ag/AgCl}$, the fracture time did not change much compared to fracture time of the samples at the corrosion potential: for the samples made from the pipe A it was equal to ~ 18.0 h, for the samples from the pipe B near ~ 19.0 h. However, an increasing of the cross-section for the samples made from the pipe A to $\sim 6.07 \text{ mm}^2$ was noted; whereas the cross-section of the

samples from the pipe B almost did not change and was equal to $\sim 3.92 \text{ mm}^2$. Under these conditions an increasing of the coefficient K_s for the metal made from the pipe A to near 1.7 was observed. For the metal of the pipe B, the value of the coefficient remained almost the same as it was at the corrosion potential, $K_s = 1.21$.

Significant changes in the fracture character were noted: for the sample made from the pipe A, a lower reduction was peculiar, which correlated with the coefficient of sensitivity to SCC (Fig. 5, *a, b*, photo 2).



a



b

Fig. 4. Mechanical fracture curves in air and corrosion-mechanical fracture curves of the X70 pipe steel samples made from the pipe A and the pipe B, in the NS4 solution under the influence of a complex of stress-corrosion factors at the potential $-1.0 V_{Ag/AgCl}$: *a* – pipe A; *b* – pipe B; 1 – sample in air, 2 – sample in the initial state, 3 – sample after cycling, 4 – sample in the initial state with LCD, 5 – sample after cycling with LCD

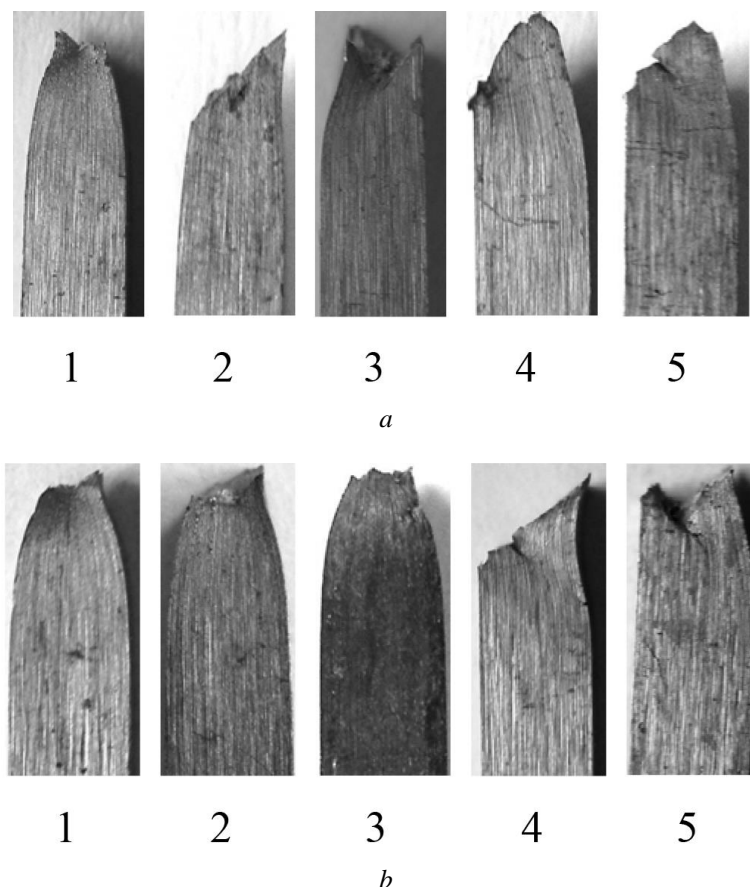


Fig. 5. Photos of fractures of the X70 pipe steel samples made from the pipe A and the pipe B after mechanical tests in air and corrosion-mechanical tests in the solution at the influence of a complex of stress-corrosion factors at the potential – $1.0 V_{Ag/AgCl}$:

a – pipe A; *b* – pipe B; 1 – sample in air, 2 – sample in the initial state, 3 – sample after cycling, 4 – sample in the initial state with LCD, 5 – sample after cycling with LCD

A preliminary cycling of the samples in the elastic region had little effect on the corrosion-mechanical properties of the samples made from the pipes A and B as compared to the initial state: the fracture time was near ~ 17.0 h and ~ 20.0 h, the cross-section area was equal to 5.94 mm^2 and 4.35 mm^2 , the coefficient was $K_s = 1.65$ for the pipe A and $K_s = 1.31$ for the pipe B. The fracture character remained ductile for the samples from the pipe B (Fig. 5, *b*, photo 3). For the samples from the pipe A a less plastic deformation is peculiar (Fig. 5, *a*, photo 3).

Similarly as at the corrosion potential, in the presence of stress concentrator, the regularities of fracture differed significantly: the fracture time significantly decreased to ~ 6.5 h (pipe A) and to 5.5 h (pipe B), the cross-section area increased to 6.34 mm^2 and 5.71 mm^2 and the degree of sensitivity to SCC was: $K_s = 1.87$ for the pipe A and $K_s = 2.13$ for the pipe B.

The fracture also took place in a different way: for the samples, a lower reduction coefficient was noted, which corresponded to the increasing in the values of the coefficient of sensitivity to SCC (Fig. 5, *a*, *b*, photo 4).

For the samples after the preliminary cycling and in the presence of LCD, the corrosion-mechanical properties were similar to those, which were on the samples without cycling and other compared to the properties of the samples in the initial state: the fracture time was ~ 2.5 h and ~ 4.5 h, the cross-section area was increase up to

$\sim 6.5 \text{ mm}^2$ and $\sim 6.37 \text{ mm}^2$, the degree of sensitivity to SCC was: for the pipe A, $K_s = 2.0$ and for the pipe B, $K_s = 2.34$. The fracture character was similar to the fracture character of the same samples without preliminary cycling (Fig. 5*a* and 5*b*, photo 5).

Thus, it was shown that at the potential – $1.0 V_{Ag/AgCl}$, which approaches the maximum protection one in accordance to DSTU 4219 [20], some differences in the sensitivity of the pipe steel to SCC, including that being under a long operation, may occur. It was assumed that higher ductile properties of the steel at the cathode potential may be associated with a lower contamination by non-metallic inclusions. But at the influence of a number of other factors, the ductility of this steel may be deteriorated, which was observed in the presence of LCD.

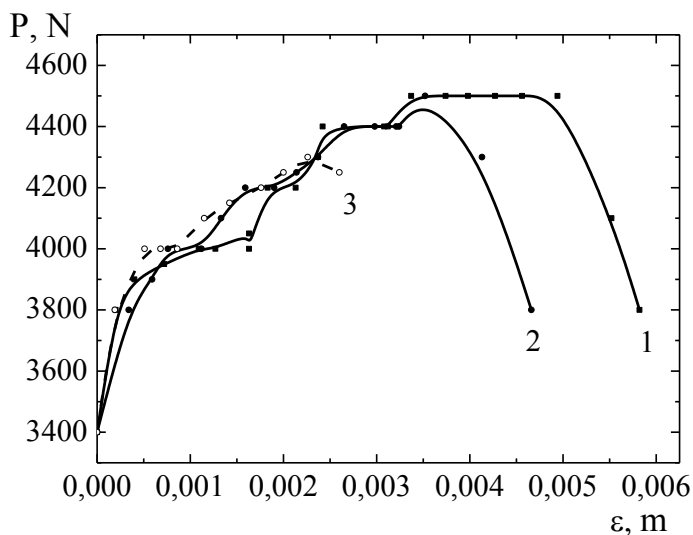
5.2.3 Investigation and estimation of the susceptibility of pipeline steel to SCC at the potential $-2.0 V_{Ag/AgCl}$

The experience showed that during operation, the increasing of the potential to higher (at the absolute value) than the maximum protection value is possible, the so-called “overprotection” phenomenon. Therefore, it was considered expedient to study the sensitivity of the pipe steel to SCC under the mentioned conditions. The curves of fracture are presented in Fig. 6, *a*, *b*.

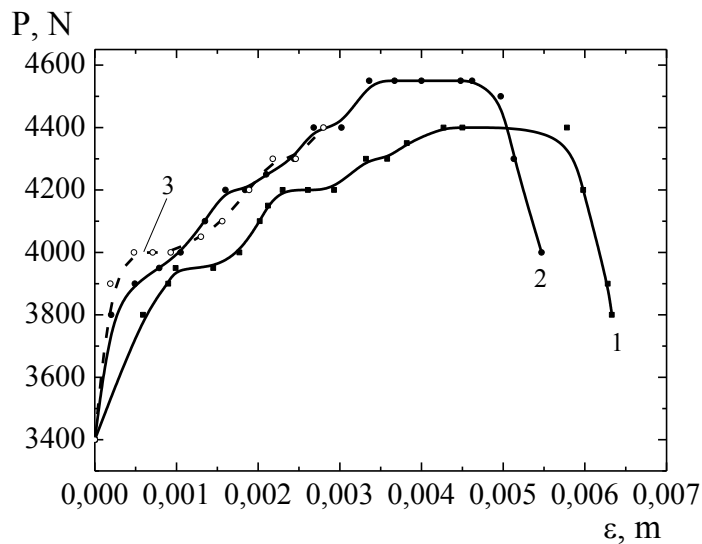
At the potential $-2.0 V_{Ag/AgCl}$, the corrosion-mechanical properties (Fig. 6a, 6b) and the character of fracture (Fig. 7, a, b) changed, which was probably predetermined by the change in the mechanism of SCC.

First, the fracture time decreased compared to the fracture time at the corrosion potential and at $-1.0 V_{Ag/AgCl}$ to ~ 14.0 h for the samples from both pipes and, accordingly, the cross-section for the samples made from

the pipe A was increased to $\sim 7.55 \text{ mm}^2$, and for the samples made from the pipe B to $\sim 6.67 \text{ mm}^2$. This naturally resulted in the increasing of sensitivity to SCC, as was evidenced by the value of K_s : for the samples made from the pipe A, $K_s=3.5$ and from the pipe B, $K_s=2.61$. The fracture of the samples of the pipes A and B occurred either almost without plastic deformation, or with a very slight reduction coefficient (Fig. 7, a, b, photo 2).



a



b

Fig. 6. Mechanical fracture curves in air and corrosion-mechanical fracture curves of the X70 pipe steel samples made from the pipe A and the pipe B, in the NS4 solution under the influence of a complex of stress-corrosion factors at the potential $-2.0 V_{Ag/AgCl}$: a – pipe A; b – pipe B; 1 – sample in air, 2 – sample in the initial state, 3 – sample after cycling, 4 – sample in the initial state with LCD, 5 – sample after cycling with LCD.



Fig. 7. Photos of fractures of the X70 pipe steel samples made from the pipe A and the pipe B after mechanical tests in air and corrosion-mechanical tests in the solution at the influence of a complex of stress-corrosive factors at the potential $-2.0 \text{ V}_{\text{Ag}/\text{AgCl}}$:

- a* – pipe A; *b* – pipe B;
- 1 – sample in air, 2 – sample in the initial state, 3 – sample after cycling,
- 4 – sample in the initial state with LCD, 5 – sample after cycling with LCD

The preliminary cycling had a little effect on the corrosion-mechanical properties of the samples made of the pipes A and B as compared to the initial state: the fracture time was $\sim 11.0 \text{ h}$ and $\sim 11.6 \text{ h}$, the cross-section area was $\sim 6.9 \text{ mm}^2$ and $\sim 7.62 \text{ mm}^2$, $K_S = 2.43$ for the pipe A and $K_S = 4.5$ for the pipe B. As in the samples without a preliminary cycling, during fracture, a plastic deformation was almost not observed (Fig. 8a and 8b, photo 3).

Thus, the shifting of the cathodic protection potential from $-1.0 \text{ V}_{\text{Ag}/\text{AgCl}}$ to $-2.0 \text{ V}_{\text{Ag}/\text{AgCl}}$ leads to changing of the fracture character of (the part of brittle component increases), which causes an increasing of the sensitivity of the pipe steel to SCC, including the samples after cycling (Fig. 8c).

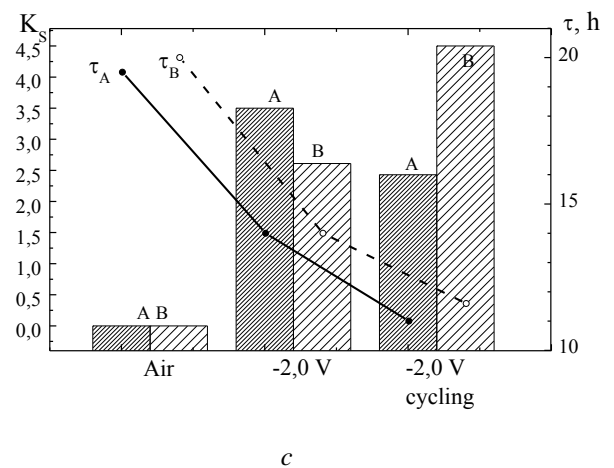
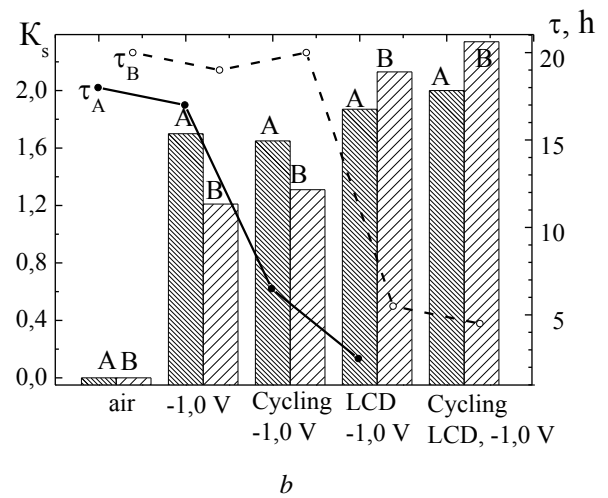
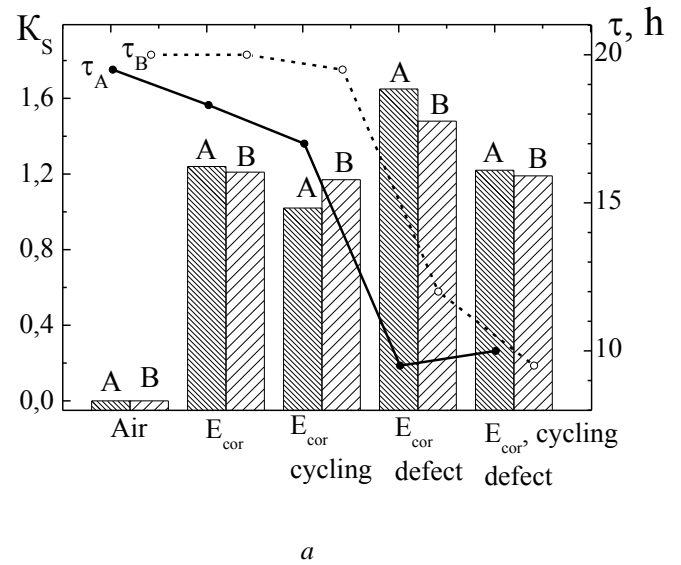


Fig. 8. Degree of susceptibility to SCC (columns) and fracture time (lines) of the X70 pipe steel samples of different manufacturers at the influence of a complex of stress-corrosion factors: *a* – at the corrosion potential; *b* – at the potential $-1.0 \text{ V}_{\text{Ag}/\text{AgCl}}$; *c* – at the potential $-2.0 \text{ V}_{\text{Ag}/\text{AgCl}}$

6. Conclusions

1. The sensitivity of the pipe steel of X70 type of a controllable rolling to SCC was investigated in the conditions of a complex influence of factors: corrosive medium, potential (E_{cor} , $-1.0 V_{Ag/AgCl}$, $-2.0 V_{Ag/AgCl}$), accumulated cyclic stresses and the presence of stress concentrator.

2. It was established that this steel under cathodic polarization is susceptible to SCC, which grows at the increasing of the potential (at the absolute value). It was shown that under a protective potential, approaching the maximum value according to DSTU 4291, some differences in the corrosion-mechanical properties of the mentioned steel may be revealed, namely: elevated or lowered sensitivity to SCC.

3. It was assumed that such features are predetermined by the contamination by non-metallic inclusions, banded orientation of the structure and grain size. At a

higher protection potential, this difference is flattened. At the same combination of other factors, the greatest influence on sensitivity to SCC is predetermined by the presence of stress concentrator.

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ВМІСТ ВАЖКИХ МЕТАЛІВ У НАФТАХ ПРИКАРПАТСЬКОЇ ТА ДНІПРОВСЬКО-ДОНЕЦЬКОЇ НАФТОГАЗОНОСНИХ ПРОВІНЦІЙ УКРАЇНИ

А. М. Єрофєєв

Наведено методику та результати дослідження вмісту важких металів у зразках нафти з двох основних нафтогазоносних провінцій України. Проведене оглядове моделювання ймовірних шляхів надходження важких металів у вуглеводневу сировину. За результатами дослідження, зроблене порівняння властивостей в залежності від хімічного вмісту зразків. Визначені ймовірні причини розбіжностей концентрації важких металів у нафтах з різних геологічних структур

Ключові слова: важкі метали, рентгенофлуоресцентна спектроскопія, геохімія нафти, хімічний склад, металоорганічні сполуки

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1. Вступ

Нафта та природні гази є важливими джерелами енергетичної та вуглеводневої сировини, що використовуються не лише для паливно-енергетичних потреб суспільства, а також для органічного синтезу матеріалів. Окрім, власне, вуглеводнів, нафти вміщують металічні хімічні елементи, що найчастіше представляють собою її мікрокомпонентний склад. Вивчення джерел та умов накопичення металів у нафтах є важливим фактором визначення генезису вуглеводнів, а також процесів забруднення навколишнього середовища. Це обумовлює актуальність проведених досліджень.

2. Літературний огляд

Проблему вмісту важких металів у нафтах почали вирішувати з середини 20 століття. Серед

останніх публікацій, присвячених цій тематиці, слід згадати як іноземні, так і вітчизняні роботи.

Ще у 2007 році була опублікована про вміст ванадію та нікелю в природних нафтах світу [1]. В ній були детально розглянуті результати досліджень концентрацій важких металів в нафтах, що стосувались фундаментальних досліджень в галузі її походження.

У 2008 році з'являється робота, присвячена ресурсній базі супутніх компонентів важких нафт [2]. В ній автор роздивився сучасний стан оцінки запасів супутніх компонентів нафти, як джерел високоякісної рідкометалічної сировини.

У 2010 році опубліковані результати дослідження глибинної зональності в збагаченності вуглеводнів важкими елементами-домішками. [3] В своїх дослідженнях автор вказує на відмінності вмісту ва-