Corrosion degradation of pipeline steels with different strength grades

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Received: 14.06.2017 Accepted: 30.06.2017

Abstract

Ukrainian gas mains steels, taking into account their age, are subjected to aging and degradation, which leads to deterioration of their properties, especially mechanical ones. Degradation of mechanical properties of steels is intensified by corrosion in the course of which hydrogen evolves and is absorbed by metal, so the metal becomes embrittled.

The aim of this work is to define susceptibility of pipeline steels with different strength grades to corrosion degradation during their long-term service. The comparative studies of corrosion and electrochemical behaviour of low alloyed gas pipeline steels with different strength grades in NS4 aqueous solution, simulating soil environment, has been carried out. Pipeline steels with three strength grades in different states – in the as-received state and after long-term operation have been investigated. The influence of long-term operation on corrosion and electrochemical properties of steels has been analysed. It has been found that the 17H1S steel (steel is equivalent to X52 strength grade) is characterized by the lowest corrosion resistance among the studied steels, and the highest corrosion resistance is typical for the X70 steel in both studied states. Corrosion and electrochemical characteristics of pipelines steels with different strength grades in the NS4 environment have been significantly deteriorated due to long-term service. It has been found out that degree of corrosion degradation caused by long-term operation of gas mains is the highest for the high strength X70 steel. Electrochemical activation of pipeline steels caused by their long-term service comes out in an increase of cathode and anode processes intensity, increase of corrosion current density, decrease of polarization resistance and in a shift of corrosion potential values towards more negative ones for degraded steels compared with steels in the initial state.

Keywords: *corrosion resistance, degradation, electrochemical properties, gas pipeline, operation.*

Introduction

Ukrainian gas transportation system is an important object for ensuring energy security of Ukraine and EU. The main gas pipelines, due to their age, are subject to aging and degradation, which causes the deterioration of their properties, first of all, mechanical ones. The degradation of the mechanical properties of the steels is intensified due to corrosion, during which the hydrogen is absorbed by the metal, and the metal becomes embrittled. The most dangerous consequence of hydrogen embrittlement of metal during its operation is a significant reduction of its resistance to brittle fracture, which may lead to rapid failure of pipeline with significant negative consequences [1, 2].

The experience of operation of gas transit pipelines indicates an increase in failures with an increase in the duration of operation due to material aging. One of the main reasons of pipeline failures is stress corrosion cracking, which is initiated from their outer surface. However, studies [3] have found that transporting of natural gas, containing residual moisture through transit pipelines is also a hydrogenated environment since electrochemical corrosion in the moisture condensed on the inner surface of the pipeline proceeds with the release of hydrogen, which is therefore absorbed and diffuses into metal. Therefore, hydrogenation of the metal of the gas pipeline during its long-term operation is possible both from the outer (in case of violation of the integrity of the protective coating) and inner surfaces. Due to the log-term mutual impact of hydrogenation and working stresses on the pipeline steel, their properties deteriorate.

The problem of aging and degradation of steels of main oil and gas transit pipelines has been extensively investigated recently. In particular, in [1, 4–7] it has been defined that prolonged exploitation of pipelines transporting a petroleum product (oil, gas, etc.) causes a significant deterioration of their mechanical properties, especially the resistance to stress corrosion cracking. However, for the integrated evaluation of the technical condition of the pipeline steels which have been operated for a long time, it is necessary to take into account their possible corrosion degradation caused both by external and internal corrosion. The results of numerous studies [8–10] have been published, concerning the determination of the effects of aggressive soil environment on resistance of pipeline steels to corrosion and stress corrosion cracking. The effect of moisture, being condensed, under transporting of natural gas, on corrosion and hydrogenation of steel from the inner surface of gas pipeline has been analyzed in [3]. It is known that pipeline wall hydrogenation

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intensifies operational degradation of metal. A series of studies are devoted to the issue of corrosion degradation of structural steels of various long-term operated responsible objects [1, 11–12].

Continuous mutual impact of the corrosion and hydrogenation factor and working stresses during operation results in pipeline steels degradation. It is important to investigate the sensitivity of pipeline steels of different strength grades to corrosion degradation during their long-term operation.

This study seeks to establish the tendency of pipeline steels of different strength grades to corrosion degradation during their long-term operation.

Materials and methods of research

The objects of research are gas pipelines steels of different strength grades: 17H1S (strength grade X52), X60 and X70 in different states – as-received and after long-term operation. Fragments of pipes being investigated were cut from main gas pipelines after different periods of their operation: 17H1S – 30 years, X60 – 25 years and X70 – 37 years. In order to compare the behavior and properties of steels, samples were also taken from stock pipes (back-ups) made of steels of various strength grades (X52, X60 and X70). Samples for electrochemical studies were cut in the form of plates and ground all surfaces. Prepared samples were degreased with acetone and applied an insulating paint coating on all sample surfaces, except for the selected electrochemical studies (area ≈0.5–0.6 cm^2) and plots for current supply.

To study the electrochemical behavior of steels and to detrmine their tendency to corrosive degradation during long-term operation, electrochemical tests have been carried out using a potentiodynamic method. The steels have been tested in NS4 aqueous solution, which, on the basis of mineralization level simulates soil environment. Corrosive solution has been treated neither during the preparation stage nor during the test itself. The temperature of the corrosive medium was 293 ± 1 K. The polarization curves have been taken on a Bio-Logic SP-300 potentiostat at the potential scanning velocity of 1 mV/s, using a standard three-electrode electrochemical cell with a saturated silver-silver chloride reference electrode and an auxiliary platinum electrode. A sample of the investigated pipeline steel has served as a working electrode .

According to the results of the tests, performed with the help of EC-Lab Express software, using the method of extrapolation of the Tafel sections of the obtained potential-dynamic polarization curves we defined basic electrochemical characteristics, such as corrosion potential E_{corr}, corrosion current density i_{corr}, the Tafel constants b_c and b_a of the cathode and anode reactions respectively. The polarization resistance R_p has been calculated in accordance with the Stern–Geary equation [13]:

$$\Delta E/\Delta i = R_p = K/i_{corr}, \quad (1)$$

where $K = b_a b_c / [2.3(b_a + b_c)]$ is a constant; b_a, b_c are the Tafel constants of the cathode and anode reactions respectively.

Study results and their discussion

Electrochemical studies have shown that the investigated pipeline steels in the initial state are characterized by active behavior in NS4 aqueous solution upon condition of natural aeration (Fig. 1) – no inactive plots has been detected on the polarization curves. The nature of the polarization curves and the intensity of the cathodic and anodic processes on 17H1S and X60 tubular steels are similar. The electrochemical behavior of X70 pipeline steel differs from other investigated steels. In particular, as it can be seen from Fig. 1 the intensity of the corrosion process of X70 steel is lower than that of 17H1S and X60 steels. The presence of boundary diffusion currents in cathode plots of polarization curves shows that the corrosion process is limited by the stage of diffusion of the depolarizer.

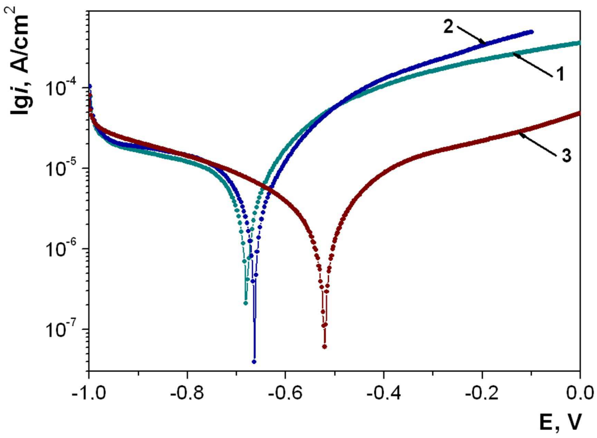

Figure 1 – Potentiodynamic polarization curves for 17H1S (1), X60 (2) and X70 (3) pipeline steels in the initial state, traced in the aqueous solution NS4

The electrochemical characteristics of the investigated pipeline steels are given in Table 1. The mechanism of corrosion is the same for all investigated steels, as evidenced by the Tafel constants whose values are close to each other. 17H1S steel with the lowest strength grade is characterized by the lowest corrosion durability: it has the highest value of corrosion current density, the lowest value of polarization resistance and the most negative value of corrosion potential (Table 1). At the same time, it should be noted that X60 steel is close to 17H1S steel according to its corrosion resistance. In particular, the values of the corrosion current density and the polarization resistance of 17H1S and X60 steels differ slightly. However, the value of the corrosion potential of 17H1S steel is more negative if compared to the X60 steel. The high-strength X70 steel has the highest corrosion resistance in NS4 aqueous solution, as evidenced by its electrochemical behavior and electrochemical parameters. It is characterized by the most positive corrosion potential value, the lowest corrosion current density value and the highest polarization resistance value.

The electrochemical behavior of pipeline steels of various strength grades in NS4 aqueous solution after their long-term (25–37 years) operation has been studied. As it can be seen from Fig. 2 the intensity of the corrosion process on the exploited steels increases significantly if compared with the steels in the initial state. Such growth can be characteristic for all the investigated steels. As a result of exploitation, the corrosion potential of steels shifts toward more negative values. In particular, the values of the corrosion potentials of X60 steel in the exploited state are about 30 mV, while the value for the X70 steel are more than 120 mV more negative than the values inherent to these steels in the initial state (Table 2). It should be noted that the corrosion potential of 17H1S steel with the least strength was almost unchanged during operation (the value of corrosion potential is –683 mV and –687 mV in the initial and exploited states, respectively).

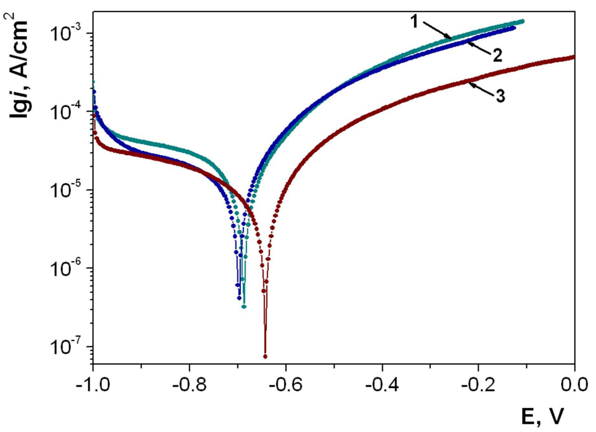

Figure 2 – Potentiodynamic polarization curves for 17H1S (1), X60 (2) and X70 (3) pipeline steels in the operational state, taken in aqueous solution NS4

Electrochemical activation of pipeline steels caused by their long-term operation results not only in the shift of the corrosion potential toward more negative values and in increase of cathode and anode reactions intensity on the exploited steels, but also in reduction of their corrosion resistance: an increase in the values of the current density of corrosion and a decrease in the values of the polarization resistance compared with the steels in the initial state (Table 1–2).

It is established that the degree of corrosion degradation caused by long-term operation is different for steels of different grades strength in NS4 aqueous solution. In particular, the degree of corrosion degradation of 17H1S and X60 steels is approximately the same, while it is the highest for a high-strength X70 steel. It can be demonstrated by the following data. The value of the corrosion current density of the exploited 17H1S and X60 steels is about 2.1–2.2 times higher than the values inherent to these steels in the initial state, but for the exploited X70 steel, the value of the corrosion current density is ≈ 3.3 times higher than for non-exploited steel. That is, high-strength steel, having the highest corrosion resistance in the initial state among the investigated steels, was subjected to corrosion degradation to a greater extent than other steels. It is also necessary to take into account different lifetimes of the investigated steels, namely that the X70 steel was used for the longest time. However, despite the significant corrosion degradation caused bylong-term operation, X70 steel is characterized by the highest resistance to corrosion in the aqueous solution of NS4 among the investigated steels. In particular, the value of the polarization resistance in this solution of the exploited X70 steel is ≈ 3.4 times lower than compared to the steel in the initial state, whereas for the exploited 17H1S and X60 steels it is 2.3–2.4 times lower than that for non-exploited. At the same time, polarization resistance value of the exploited X70 steel is the highest (6,92 kOhm·cm^2), while the same values for 17H1S and X60 steels are significantly lower (3.53 kOhm·cm^2 and 3.89 kOhm·cm^2 respectively).

It should also be noted that the value of the Tafel constant of the cathode reaction was practically unchanged for X60 and X70 steels and somewhat decreased for 17H1S steel. As for the Tafel constant of the anode reaction, its value practically did not change for X70 steel and slightly decreased for 17H1S and X60

Table 1 – Electrochemical characteristics of pipeline steels of different strength in the initial state in NS4 solution

Steel	Corrosion potential E_{corr}, mV	Corrosion current density i_{corr}, μA/cm^2	Tafel constants, mV		Polarization resistance R_p, kOhm ·cm^2
			b_c	b_a	
17H1S	-683	1.85	–90	62	8.63
X60	-664	1.81	–90	63	8.90
X70	-518	0.67	–89	61	23.49

Table 2 – Electrochemical characteristics of in-service pipeline steels with different strength in NS4 solution

Steel	Corrosion potential E_{corr}, mV	Corrosion current density i_{corr}, μA/cm^2	Tafel constants, mV		Polarization resistance R_p, kOhm ·cm^2
			b_c	b_a	
17H1S	-687	4.20	–83	58	3.53
X60	-696	3.86	–90	56	3.89
X70	-642	2.24	–88	60	6.92

steels. The obtained data indicate that the anode reactions on the exploited 17H1S and X60 steels and the cathode reactions on 17H1S steel (Table 2) occure easier to compare with the steels in the initial state.

Thus, such electrochemical characteristics of steel as the corrosion current density and polarization resistance are the most sensitive to the operational degradation.

However one more pecularity of electrochemical behavior of investigated pipeline steels should be noted. In particular, 17H1S and X60 steels are characterized by easier activation of the anode process in the NS4 aqueous solution compared with X70 steel when the same overvoltage is applied (Fig. 3). Meanwhile, the degree of such activation is practically identical for lower strength steels. That is, 17H1S and X60 steels will corrode first.

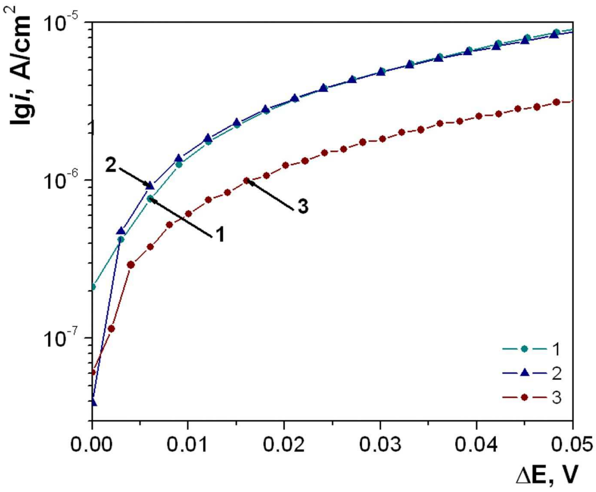

Figure 3 – ΔE – lg*i* dependencies for 17H1S (1), X60 (2) and X70 (3) pipeline steels in the initial state in the NS4 aqueous solution at the same anodic overvoltage ($\Delta E = E_{pol} - E_{corr}$, E_{pol} – anodic polarization potential)

The revealed regularity is maintained also for exploited steels – at the same overvoltage, the anode reaction of the dissolution of the exploited steel X70 (Fig. 4) is the least among the investigated steels. However, the difference in the degree of such activation for high strength steel X70 and steels with lower strength after long-term operation is reduced. In particular, at an anodic overvoltage of 50 mV, the value of the resulting anode current density for the steel X70 in the initial state is ~ 2.8 times lower than its value for 17H1S and X60 steels, and for the exploited steel, this ratio decreaded and equals ~ 1.9 times.

Consequently, the deterioration of a number of corrosion and electrochemical characteristics of exploited pipeline steels of different strength grades, especially corrosion current density and polarization resistance indicates their corrosion degradation, which is evidently caused by operational degradation due to the long-term mutual effect of corrosion hydrogenation environments and working stresses during their exploitation.

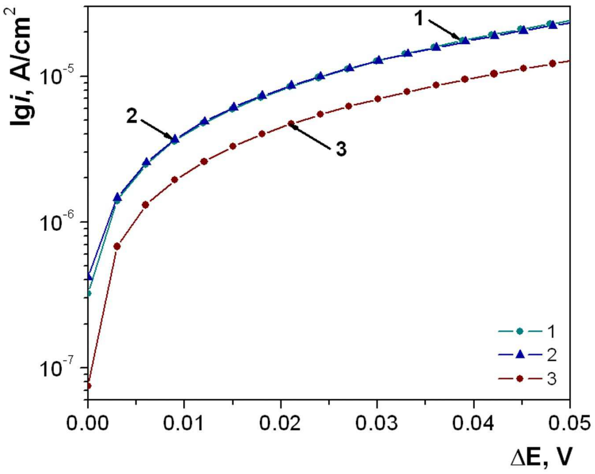

Figure 4 – ΔE – lg*i* dependencies for 17H1S (1), X60 (2) and X70 (3) pipeline steels in the operated state in the NS4 aqueous solution at the same anodic overvoltage ($\Delta E = E_{pol} - E_{corr}$, E_{pol} – anodic polarization potential)

Conclusions

Susceptibility of low-alloyed steels of gas pipelines of different strength grades in different states (the as-received state and after long-term operation) to corrosion degradation in the course of long-term operation has been established by comparative studies of their corrosion and electrochemical behavior in the NS4 aqueous solution, simulating soil environment. It was found that the high-strength X70 steel is characterized by highest corrosion resistance among the investigated steels, both in the as-received state and after long-term operation. Long-term operation causes a significant deterioration of the corrosion and electrochemical characteristics of pipeline steels of different strength grades in NS4 environment. It has been established that the degree of corrosion degradation caused by long-term operation of gas pipelines is the highest for high-strength X70 steel. Electrochemical activation of pipeline steels caused by their long-term service comes out in an increase of cathode and anode processes intensity, increase of corrosion current density, decrease of polarization resistance and in a shift of corrosion potential values towards more negative ones for degraded steels compared with steels in the as-received state.

The research has been supported by the NATO in the Science for Peace and Security Programme under the Project G5055.

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УДК 620.193

Деградація корозії трубопровідних сталей різної міцності

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Сталі магістральних газопроводів України, зважаючи на їх вік, піддаються старінню та деградації, що зумовлює погіршення їх властивостей, перш за все, механічних. Деградацію механічних властивостей сталей інтенсифікує корозія, під час перебігу якої виділяється водень, що абсорбується металом, і метал окрихчується.

Ця робота спрямована на встановлення схильності трубних сталей різної міцності до корозійної деградації у процесі їх тривалої експлуатації. Проведено комплекс порівняльних досліджень корозійно-електрохімічної поведінки низьколегованих трубних сталей газопроводів різних класів міцності у водному розчині NS4, що імітує ґрунтове середовище. Досліджено трубні сталі трьох класів міцності у різних станах – вихідному та після тривалої експлуатації. Проаналізовано вплив тривалої експлуатації на корозійно-електрохімічні властивості сталей. Встановлено, що серед досліджених сталей найнижчою корозивною тривкістю характеризується сталь 17Г1С (сталь групи міцності Х52), а найвищою корозивною тривкістю володіє сталь Х70 в обох досліджених станах. Внаслідок тривалої експлуатації суттєво погіршуються корозійно-електрохімічні характеристики трубних сталей різних класів міцності у середовищі NS4. Виявлено, що ступінь корозійної деградації, спричиненої тривалою експлуатацією магістральних газопроводів, є найвищим для високоміцної сталі Х70. Електрохімічна активація трубних сталей, зумовлена їх тривалою експлуатацією, проявляється у зростанні інтенсивності протікання катодних та анодних процесів на експлуатованих сталях, збільшенні густини струму корозії, зниженні поляризаційного опору та зміщенні потенціалу корозії у бік від’ємніших значень для деградованих сталей порівняно зі сталями у вихідному стані.

Ключові слова: *газопровід, деградація, експлуатація, електрохімічні властивості, корозійна тривкість*.