INFLUENCE OF STRENGTH PROPERTIES OF PIPE STEEL ON ITS CORROSION RESISTANCE AND ELECTROCHEMICAL CHARACTERISTICS IN SOLUTIONS OF DIFFERENT CORROSIVITY

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Pipes from high strength steel are applied both in extractive industry and in gas transportation system. A complex of research presented in this work, is aimed at obtaining comparative data on corrosion resistance of steel of different strength classes in order to analyze the prospects for application of high-strength steel under various corrosive conditions.

It was found that in the neutral and weakly alkaline solutions the rate of total corrosion of X80 steel with increased strength characteristics is somewhat higher, compared with X70. In an alkaline solution with activator ions in which the local process can occur, the rate of total corrosion of X80 steel is almost two times smaller than that of X70 steel. It was shown that in solutions of different corrosivity under the conditions of free oxygen access at polarization, steel strengthening promotes acceleration of anodic dissolution to a certain extent. However, the mechanism of anodic dissolution remains unchanged. At cathode polarization facilitation of hydrogen evolution in these solutions on X80 steel should be taken into account while selecting the maximum protective potentials of steel pipes.

One of the main strategic way of developing the pipe production at the present stage and the pipeline transport, in particular, is finding a solution to the problem of safety and reliability of pipeline system operation. These problems can be solved under the conditions which guarantee the required level of consumer properties of pipe products. Steel pipelines, including those from high strength steel, are exposed to complex stress-strain impact under real operation conditions, which promotes the wall corrosion. Cathodic polarization which is applied for electrochemical protection of the main pipelines at -1.0 V (SCE) potential in environments with pH close to the neutral ones promotes metal hydrogenation that becomes more intensive in the case of application of tensile stresses, and promotes loss of steel ductility the more, the higher its strength [1-5]. Inclusions in steel, enriched in aluminium, titanium,

silicon oxide, iron carbide, and dislocations are traps for hydrogen atoms; they can promote crack initiation, even in the absence of external tension and their location predominantly near these inclusions [6-7]. As a rule, at pH close to the neutral ones, the mechanism of electrochemical corrosion of welded joints of steel, in particular, higher strength ones, does not change essentially, either at hydrogenation or at stress application or at combined impact of both the factors: hydrogenation just changes local activity of welded joint dissolution, stress increase and promotes acceleration of the anodic process in the crack tip [9].

The purpose of the work consisted in studying the influence of strength characteristics of pipe steel on corrosion and electrochemical properties.

Research methodology

The object of study was pipe steel of strength class X70 and X80.

Investigations were carried out in the following solutions:

- 3 % NaCl (pH 6,6, electric conductivity 90.0×10^{-3} S/cm);

- model soil electrolyte of the following composition, g/l: 0.037 KCl + 0.559 $NaHCO_3$ + 0.008 $CaCl_2$ + 0.089 $MgSO_4$ (pH 8.2, electric conductivity was 1.7×10^{-6} 0.087 S/cm), furtheron referred to as MSE;

- 0.1M $NaHCO_3$ + 0.1M Na_2CO_3 + 0.002M NaCl (pH 9.8, electric conductivity was 46.6×10^{-3} 0.087 S/cm).

Investigations were performed using standard methods: measurement of mass, potentiometry and polarization curve method. The following measuring equipment was used during investigations: analytical scale VRL 200, thermal chamber MLW 117-0200, and potentiostat PI-50.

The method of mass measurement allows determination of corrosion rate i_c in the environment under investigation by sample mass loss. Studies in each of the environments were conducted in parallel on three rectangular plates. After degreasing, the samples were soaked in thermal chamber MLW 117-0200 at the temperature of plus (105-110) C up to constant mass, weighed in analytical scales VRL-200 g of 2nd class of accuracy, and their area was determined with an electronic caliper. Total time of sample soaking in the environments under investigation was approximately 1000 h.

After testing, the samples were washed in running water, corrosion products were removed with rubber, rinsed with distilled water and dried on filter paper, then dried as mentioned above, and weighed.

Proceeding from change of sample mass and duration of studies, corrosion rate (K) expressed in g/(m²·h) was found by the following formula:

$$K = \frac{\Delta m}{ST}, \qquad (1)$$

where Δm are the corrosion losses of the sample, g;

S is the sample surface area, m^2;

T is the duration of investigations, hours.

Corrosion penetration rate (P) in mm/year under the conditions of uniform corrosion was found from the following formula:

$$P = \frac{K \cdot 10^{-3}}{d} \qquad (2)$$

where K is the corrosion rate, $g/m^2 \cdot year$;

d is the metal density, g/cm^3.

Corrosion potentials of steels were studied in the above-mentioned solutions for 1 hour, using a PI-50 potentiostat.

The method of polarization curves was applied to study the peculiarities of electrochemical properties of steel by analysis of general dependence of the rates of anode and cathode reaction on potential. Potentiodynamic mode and rate of potential change of 5×10^{-4} V/s were applied.

Samples of steel under investigation were soaked in this environment for 1 hour, until the stationary value of corrosion potential has been reached. The working electrodes were samples of X70 and X80 steel, the reference electrode was a silver chloride electrode, and the counter electrode was platinum.

Anode curves were measured from corrosion potential up to potential more positive than that of oxygen evolution from water solutions, and cathode curves were measured from corrosion potential up to potential which is more negative than that of the start of hydrogen evolution. Investigation results were presented in semi-logarithmic coordinates "lg I – E", where i is the current density per unit of sample surface, E is the potential. General nature of the dependence of the rate of anode and cathode reactions on potential and electrochemical parameters characterizing these processes, were analyzed.

Results and Discussion

Chemical composition and mechanical properties of pipe steel of X70 and X80 type are given in Tables 1 and 2.

Table 1. Composition of studied steels

Steel grade	Weight fraction elements, %							
	C	Mn	V	Nb	Ti	Cu	Mo	Cr
X70	0.08	1.52	0.036	0.039	0.018	0.05	0.015	0.03
X80	0.06	1.64	0.036	0.040	0.015	0.07	0.012	0.03

Table 2. Mechanical properties of studied steels

Steel grade	σ_Y, MPa	σ_T, MPa	KV^{-10}, MPa
X70	535	640	145…210
X80	625	691	285…308

Results of corrosion studies revealed that in all the studied solutions black-coloured corrosion products formed on the samples, which uniformly covered the surface, no pitting or corrosion spots were found, and the nature of corrosion was evaluated as total uniform, in keeping with GOST 9.908.

In 3% NaCl and MSE the rate of total corrosion of X80 steel is slightly higher, compared to X70 steel (0.0324 mm/year for X80 and 0.0289 mm/year for X70, and 0.0227 mm/year for X80 and 0.0216 mm/year for X70, respectively). In 0.1M $NaHCO_3$ + 0.1M Na_2CO_3 + 0.002M NaCl solution, in which the local process can proceed on condition of surface passivating, the rate of total corrosion of X80 steel is almost two times smaller, than that of X70 steel (0.000036 mm/year for X80 and 0.000063 m/year for X70), Fig. 1, a.

Thus, in the neutral and weakly alkaline solutions the rate of corrosion of X70 steel is slightly higher, compared to X70 steel. In the solution, in which the local process can proceed on condition of surface passivating, the rate of total corrosion of X80 steel is almost two times smaller than that of X70 steel.

It is known that electrochemical methods are applied to obtain initial information on material properties, which are some of the most common express-methods of investigation. So, comparing and analyzing the values of corrosion potential and pitting, anodic dissolution currents in the active and passive regions, limiting diffusion current of oxygen reduction, potentials of corrosion and start of hydrogen evolution for different metals, alloys and zones of welded joints in environments under investigation, it is possible to obtain preliminary data on their corrosive activity. Methods for potentiometry and polarization curves were applied, when comparing the features of electrochemical behaviour of steels of X70 and X80 type.

Fig. 1, b gives the corrosion potentials of the studied steels in environments with different aggressiveness.

It follows from experimental data that in neutral environment the values of corrosion potentials of both the steels practically coincide, and in weakly alkaline one the surface of steel X80 is in a somewhat more passive state than that of X70, whereas in alkaline solution with additives of activator ions a violation of continuity of passive film for X80 steel is observed which is accompanied by shifting of corrosion potential in the negative direction, compared to steel X70.
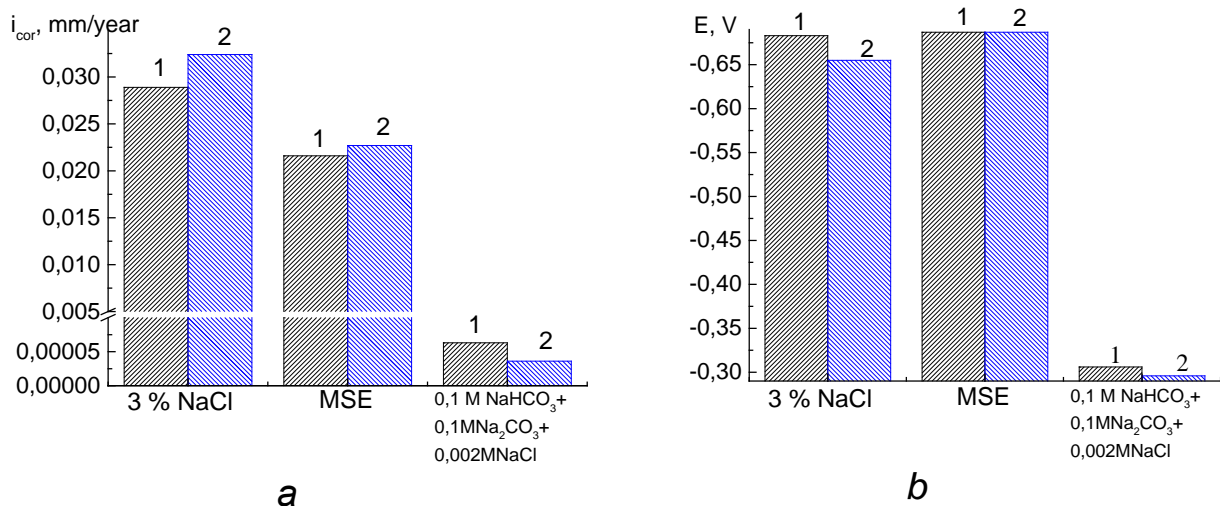

Fig. 1. Corrosion rate (a) and corrosion potentials (b) of pipe steel X70 (1) and X80 (2) at room temperature in solutions under investigation

It is anticipated that when polarization is induced, the regularities of corrosion behaviour can be different.

Fig. 2 gives polarization curves for X70 and X80 steel in solutions of different aggressiveness under the conditions of free access of oxygen.
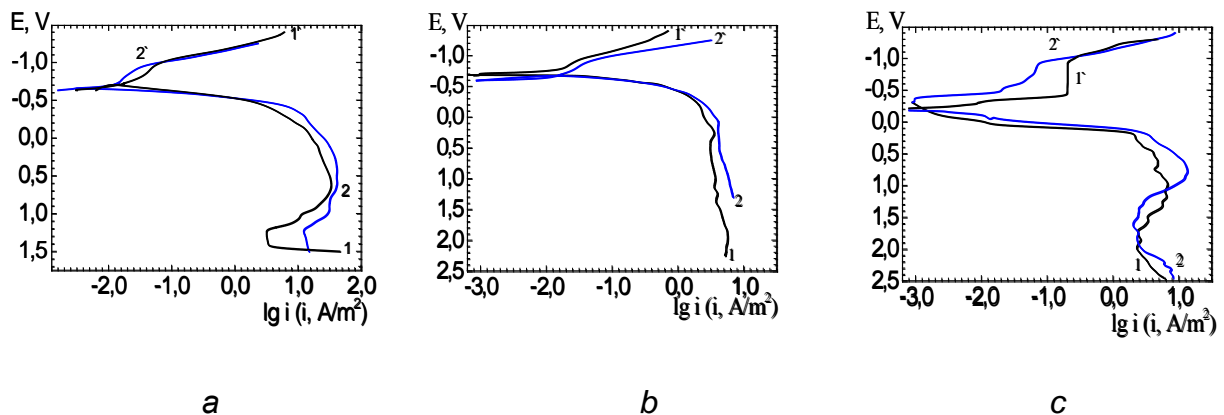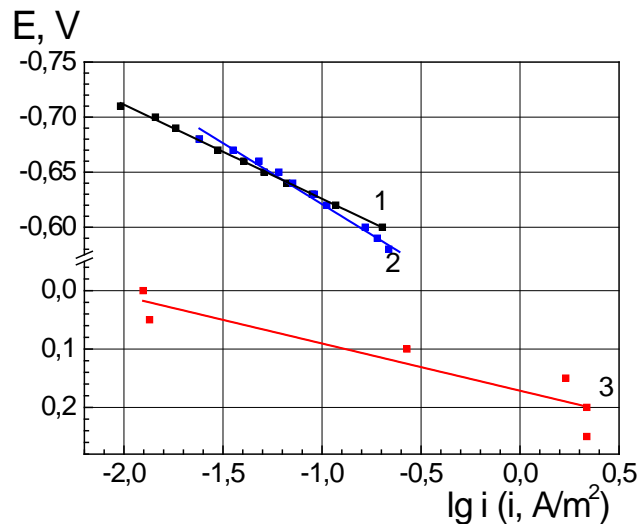

Fig. 2. Polarization curves of pipe steel X70 (1) and X80 (2) at room temperature in solutions under investigation: a – 3 % NaCl, b – MSE, c – 0.1M Na_2CO_3+0.1M $NaHCO_3$+0.002 NaCl

The following similar regularities are noted:
- regularities of anode and cathode behaviour do not differ in a broad range of potentials;
- in the region of active anodic dissolution the curves practically coincide and have almost the same slopes that is indicative of diffusion control of anodic dissolution reaction;
- for X80 steel at anodic polarization the region of active anodic dissolution is much larger and for this steel somewhat higher current values are characteristic in the entire range of potentials;
- in all the solutions at the established rate of potential change, the region of persistent passivating was not observed, so current density in the passive region was not determined.

For active dissolution region, anode curve slopes were calculated, using Origin programs, Fig. 3.

a
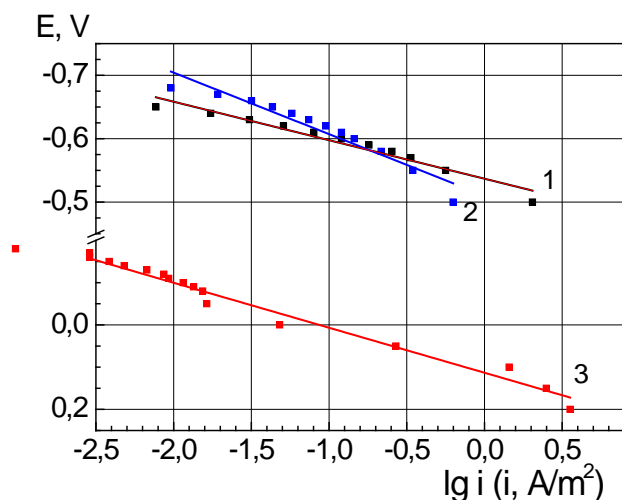
b

Fig. 3. *Tafel areas of anodic polarization curves of pipe steel X70 (a) and X80 (b) at room temperature in solutions under investigation:*
1 – 3 % NaCl, 2 – MSE, 3 – 0.1M Na_2CO_3+0.1M $NaHCO_3$+0.002 NaCl

Analyzing the nature of anode curves of X70 and X80 steels in a broad range of potentials in 3% NaCl solution (Fig. 2, a) we can note that after the region of active anodic dissolution, the length of which was approximately 0.185 V (from corrosion potential up to potential of approximately -0.500 V) for steel X70 and 0.255 V (from corrosion potential up to potential of approximately -0.400 V) for X80 steel, a region was found, in which the process of active anodic dissolution was decelerated, as a result of formation and staying of corrosion products on the sample surface. After that anodic dissolution proceed at much smaller rate. Calculated values of Tafel slopes for X70 and X80 steel were equal to approximately 0.085 V and 0.054 V. This is a confirmation of the fact that the rate of anodic dissolution of both the steels is controlled by bringing dissolved oxygen to the surface, and removing the corrosion products. Somewhat higher Tafel slope values for X70 steel are attributable to formation of a denser layer of corrosion products, through which supplying oxygen to corroding surface becomes difficult. As is seen from comparison of anode curves (Fig. 2, a – curves 1 and 2), the region of active dissolution of X70 steel is somewhat shorter than that of X80 that also confirms the expressed assumption as to possible formation of a denser layer of corrosion products on X70 steel, compared to X80 steel, and correlates with the results obtained by the method of measurement of mass.

It follows from analysis of cathode curves that:

- limiting current of oxygen reduction on X70 steel is almost 4 times higher than that for X80 steel (3.98×10^{-2} A/m^2 and 1.35×10^{-2} A/m^2, respectively), that may promote greater susceptibility of X80 steel to hydrogenation in this solution;

- potentials of the start of hydrogen evolution are almost the same and equal to -0.950 V for X70 and to -0.940 V for X80;

- rate of active evolution of oxygen on both steels practically coincides (cathode polarization curves in the region of active evolution of oxygen coincide at potentials more negative than -1.0 V,).

In MSE, Fig. 2, b, the region of active anodic dissolution of X70 steel was close to 0.110 V (from corrosion potential up to potential of approximately -0.570 V) for X70 steel and 0.170 V (from corrosion potential up to potential of approximately -0.500 V) for X80. Similar to 3% NaCl solution, a region is observed, in which the process of active anodic dissolution is decelerated. Tafel slopes of anodic polarization curves of both the steels are somewhat overestimated, probably as a result of more difficult supply of oxygen to the corroding surface, and are equal to approximately 0.111 V for X70 ad 0.074 V for X80.

Analysis of cathode curves leads to the following conclusions;

- limiting current of oxygen reduction on X80 steel is somewhat higher than that on X70 steel (2.50×10^{-2} A/m² and 2.63×10^{-2} A/m², respectively);

- potential of the start of hydrogen evolution on {80 steel is almost 0.1 V smaller by absolute value than that of X70 steel, - 0.85 V and – 0.95 V, respectively;

- rate of active evolution of hydrogen on X80 steel is also lower than that on X70 steel.

In alkaline environment with additives of activator ion the region of active dissolution of X80 steel is equal to approximately 0.096 V (from corrosion potential up to 0.2 V), for X70 it is almost 0.106 V (from corrosion potential up to 0.2 V), Fig. 2, c. In the region of potentials from -0.2 V up to 2.0 V deceleration of active anodic dissolution is noted, which is due to surface shielding by corrosion products that formed at anodic polarization. In this environment the effect of deceleration of the anodic process on X80 steel was more pronounced at the same anodic potential, and consisted in reduction of anode currents by a value greater than an order of magnitude.

Analysis of anode curves shows that:

- limiting current of oxygen reduction on X80 steel is 3.6 times smaller than on steel X70 (6.30×10^{-2} A/m² and 1.76×10^{-2} A/m², respectively)$

- potential of the start of hydrogen evolution on X80 steel is almost 0.05 V smaller by absolute value, than that of X70 steel – 0.850 V and – 0.900 V, respectively.

Conclusions

Proceeding from results of corrosion studies it was established that in 3% NaC (pH 7) and in model soil electrolyte (pH 8.2) the rate of continuous corrosion of X80 steel is slightly higher than that of X70 steel (0.0324 mm/year for X80 and 0.0289 mm/year from X70 and 0.0227 mm/year for X80 and 0.0216 mm/year for X70, respectively). In 0.1M $NaHCO_3$ + 0.1M Na_2CO_3 + 0.002M NaCl (pH 9.8) solution, in which local process can run on condition of surface passivating, the rate of continuous corrosion of X80 steel is almost two times smaller, than that of X70 steel (0.000036 mm/year for X80 and 0.000063 mm/year for X70).

Under the conditions of free access of oxygen at polarization, steel strengthening to a certain extent promotes acceleration of the rate of anodic dissolution, while its mechanism remains the same. Facilitation of hydrogen evolution at steel strengthening is noted:

- in 3 % NaCl – from -0.940 V for X80 up to -0.950 V for X70,

- in model soil electrolyte – from -0.850 V for X80 up to -0.950 V for X70,

in 0.1M $NaHCO_3$ + 0.1M Na_2CO_3 + 0.002M NaCl – from -0.850 V for X80 up to -0.900 V for X70, that should be taken into account during selection of maximum protective potentials of pipes from this steel.

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