PHYSICAL-CHEMICAL, MECHANICAL AND OPERATIONAL TESTS OF OIL AND GAS PIPES OF INCREASED CORROSION RESISTANCE

Introduction. One of the main reasons for the failure of pipes and other equipment operated in the oil and gas industry is metal corrosion caused by the presence of heterogeneous liquid and corrosively active components in formation waters and well products that surround them: chlorides, carbon dioxide, hydrogen sulfide \[1−3\]. Corrosion significantly shortens the useful life of equipment, leads to accidents in oil and gas industries, causes significant economic losses and pollutes the environment \[1−5\]. The most susceptible to corrosion are pump-compressor pipes (PCP), because they are in the most difficult conditions during operation. At the same time, the vast majority of destruction occurs along the thread \[1, 5\]. Therefore, the reliability and durability of equipment at oil and gas fields is determined by the rational choice of structural materials and pipe manufacturing technologies.

The literature analysis shows that, depending on the aggressiveness of the environment in the well, it is economically feasible to use pipes of increased and high corrosion resistance, made of low-alloy steels containing up to 2% Cr, of stainless high-chromium, chromium-nickel, and chromium-nickel-molybdenum steels and alloys \[5−10\], as well as with protective anti-corrosion coatings. In environments with an increased content (up to 4...6%) of chlorides and a partial pressure of carbon dioxide up to 30 MPa at temperatures up to 150°C quite corrosion-resistant turned out to be pipes made of martensitic steels with 9...12% Cr \[5, 11\]. With a higher content of chlorine ions in the environment, especially in conditions of high temperatures and CO\(_2\) pressure, pipes made of ferritic-austenitic (duplex) steels are more corrosion-resistant \[12-15\], and in deposits that contain hydrogen sulfide and carbon dioxide at a partial pressure of up to 30 MPa each and a temperature of up to 200°C, – tubing made of austenitic Cr – Ni – Mo alloys \[15, 16\].

One of the effective ways to increase the operational reliability of pipes with threaded ends, in particular, tubing, is the use of anti-corrosion coatings that can provide threads and threaded connections with high corrosion and erosion resistance, wear resistance and tightness during operation. The analysis of the literature showed the advantage of thermodiffusion iron-zinc coatings obtained in powder mixtures, as they have increased resistance against the corrosive and
erosive effects of an aggressive water environment due to the appropriate structure, increased hardness and other special properties [1, 5, 17-19]. Recently, the development of a new generation of coatings has begun, which are a duplex system - a combination of a metal coating (from zinc, zinc-aluminum or iron-zinc alloy) with an organic coating applied to it, which, thanks to a synergistic effect, provides optimal anti-corrosion properties to the steel product in aggressive environments [5].

The purpose of the work was to study the qualitative characteristics of oil and gas pipeline (smooth) and pump-compressor (threaded) pipes of increased and high corrosion resistance, manufactured according to the developed technologies, and to provide recommendations for their rational use in the oil and gas production industry in environments of various corrosion activity.

Research materials and methods. Pipes made of steels of various degrees of alloying, manufactured according to the developed technologies, were studied: oil and gas pipelines made of low-alloy steel 06Cr1 of corrected chemical composition; pump-compressor (threaded) pipes made of high-alloy martensitic (20Cr13), ferritic-austenitic (02Cr22Ni5Mo3) steels and austenitic chrome-nickel-molybdenum alloy, as well as pipes with a protective anti-corrosion thermodiffusion iron-zinc coating.

The microstructure of steels and protective coatings was studied by the methods of light metallography and electron microscopy. Attention was paid to the definition and quantitative assessment of special low-energy grain boundaries (SG) in the theory of coincident site lattices (CSL). Corrosion tests of the pipes were carried out in laboratory conditions by gravimetric and electrochemical methods in environments inherent in the oil and gas production industry: chloride, chloride-acetate solutions, in a solution of sulfuric acid and thiourea, as well as for resistance to sulfide stress corrosion cracking (SSCC) and hydrogen cracking (HC). according to the methods of NACE TM 0177 and NACE TM 0284. Industrial tests of pipes were carried out in highly mineralized reservoir water at oil and gas fields of Ukraine.

The mechanical properties of the pipes were tested for tension and impact bending by standard methods.

Research results and their discussion. Oil and gas pipelines made of steel 06Cr1. Complex metallographic, corrosion, mechanical and operational studies established the following.

Oil and gas pipelines made of 06Cr1 steel, due to the application of the principle of grain-boundary engineering (GBE) of polycrystalline materials [18] in their manufacture, were characterized by a fine-grained ferrite-pearlite structure with an increased content of special low-energy grain boundaries (SB) in ferrite (Fig. 1) and low-energy ferrite-pearlite interphase boundaries.

Due to the selected chemical composition and structure of steel, pipes made of steel 06Cr1 had a significant advantage in corrosion resistance compared to pipes made of steel 20 according to GOST 8732, which are still used in the oil and gas industry, namely [4-10]:

- 40 times lower corrosion rate when testing samples by the gravimetric method for 1,500 h in a model chloride-acetate solution of 0.1N NaCl + 0.5 g/l CH₃COOH and the ability to passivate (Fig. 2);

Fig. 1. Microstructure of oil and gas pipelines made of steel 06X1, special boundaries in ferrite are marked by arrows
- a significantly lower tendency to flooding in the process of cathodic polarization of samples in a solution of sulfuric acid and thiourea 1N H₂SO₄ + 1.5 g/l CS(NH₂)₂, in particular, a 5 times lower cathodic current density (Lg Iₖ) after holding for 4 h at potential E = −1.2 V;
- 2.7 times lower corrosion rate during the hydrogen cracking test (CR);
- were characterized by an almost 250-fold decrease in the dissolution current (Lg Iₐ) on the anodic polarization curve in a 0.1 N NaCl solution after long-term operation in an oil field in highly mineralized formation water.

During operational tests at an oil and gas field for 6 years, the average corrosion rate of pipes made of 06X1 steel was 0.052 mm/year.

The mechanical properties of pipes made of 06X1 steel correspond to the X42-X46 strength group according to the API 5L standard of the American Petroleum Institute and are characterized by high plasticity, including impact strength at negative temperatures (Table 1).

**Table 1.**

<table>
<thead>
<tr>
<th>Tube size, mm</th>
<th>σₚ, MPa</th>
<th>σ₀,₂, MPa</th>
<th>σ₀,₂ / σₚ</th>
<th>δₖ, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>∅ 76...114x6...9</td>
<td>420...460</td>
<td>300...345</td>
<td>0.71...0.75</td>
<td>32...37</td>
</tr>
<tr>
<td>Requirements of API 5L to tubes of X 42 / X 46 strength groups</td>
<td>not less than</td>
<td>not more than</td>
<td>not less than</td>
<td></td>
</tr>
<tr>
<td>42 / 441</td>
<td>294 / 322</td>
<td>0.93</td>
<td>23 / 22</td>
<td></td>
</tr>
</tbody>
</table>

Heat treatment of pipes according to the developed technology contributed to the improvement of the steel structure due to the release of finely dispersed chromium carbides in the ferritic base, and also increased the strength of the pipes to group X 56 according to API 5L and resistance to SSCC.

**Pipes made of high-alloy steels.** The results of research on pump-compressor pipes made of high-alloy steels showed the following [11-16].

Pipes made of 20Cr13 steel had a martensitic structure after pressing; during the next tempering in the temperature range of 600...800°C, the martensite disintegrated into a ferrite-carbide mixture. The mechanical properties of the pipes after tempering according to the developed regimes corresponded to strength groups L80...P110 according to the API 5CT standard (for threaded pipes).

Hot-pressed pipes made of duplex steel 02Cr22Ni5NMo3 were characterized by a two-phase fine-grained structure with an elongated austenite phase in the ferrite base in the direction of deformation. Heat treatment of pipes according to the developed technology of double hardening, based on the principle of GBE [9], ensured obtaining an optimal structure of steel with
an increased content of special low-energy grain boundaries in the austenitic and ferritic phases (Fig. 3).

Mechanical properties of pipes made of duplex steels corresponded to the group N 80 (API 5CT): \( \sigma_b = (760...765) \text{ MPa} \), \( \sigma_{0.2} = (563...568) \text{ MPa} \), \( \delta = (35...38)\% \), \( \psi = (77...79) \% \), \( KCV = (285...289) \text{ J/cm}^2 \).

Fig. 3. Microstructure of pipes made of ferritic-austenitic steel 02X22H5AM3, prepared using new technology, \( \times 1000 \); sign: ● – SG \( \Sigma 3 \) CSL at \( \gamma \)-phase; ○ – borders of the general type

The microstructure of pipes made of the 03Cr25Ni30Mo3Nb alloy was represented by recrystallized austenite grains No. 6-7 according to GOST 5639 with an increased content of special low-energy twin boundaries \( \Sigma 3 \) (CSL), Fig. 4.

Fig. 4. Microstructure of pipes made of steel 02Kh25N22AM2: arrows show coherent SG \( \Sigma 3 \) CSL; arrow from No. 1 – facets on SG \( \Sigma 3 \); circles 2 circle characteristic multiple joints, \( \times 500 \)

The level of mechanical properties corresponded to strength group L 80 according to the API 5ST standard. A further increase in the strength of such pipes can be achieved only by their subsequent cold deformation.

Tests of samples of pipes made of duplex steel 03Cr22Ni5NMo3 and austenitic alloy 03Cr25Ni30Mo3Nb for resistance against SSCC and against general corrosion in a hydrogen sulfide-containing solution according to the NACE TM 0177 method solution have established that they are not prone to corrosion cracking under tensile stresses \( \sigma = 0.9 \sigma_{0.2} \) and \( \sigma = \sigma_{0.2} \), respectively. The corrosion rate of duplex steel pipes was 0.005 mm/year, and of Cr-Ni-Mo alloy pipes was 0.00048 mm/year. Therefore, despite the high cost of pipes made of high-alloyed steels, their use in highly aggressive environments with a high content of carbon dioxide and hydrogen sulfide is considered economically feasible, because over time it gives a significant profit due to savings on the operation of wells.
Studies of thermodiffusion iron-zinc coatings with increased corrosion resistance and wear resistance showed their unique properties [1; 5; 17]. They are caused by the structure of the coating and interpenetration and a uniform change in the concentrations of zinc and iron throughout the thickness of the coating with its maximum content in the outer layers. This ensures satisfactory plasticity, high corrosion resistance of the tread type, the effect of solid lubrication in threaded pipe joints and high tightness during multiple (up to 20...30 or more) screwing-unscrewing operations required in the process of well operation. The advantages of the protective thermodiffusion iron-zinc coating are also its high resistance to mechanical damage, the absence of corrosion centers in the event of artificial damage to the coating, and the reliability of the resource of threaded joints.

The results of long-term (for 5.5 years) industrial tests of a batch of diffusion-galvanizaned pipelines (with the initial thickness of the coating layer on the inner and outer surfaces of 35...65 μm) at the oil wells of Oil and Gas Production Administration «Poltavaftogaz», Public Joint Stock Company «Ukronta», with periodic lifting of pipe columns and inspections of the pipes showed that during operation the coating remained on the surface of the pipes and retained its protective anti-corrosion and anti-erosion properties. Unscrewing of pipes with a diffusion zinc coating, in contrast to pipes without coating, occurred without damage to the thread.

A promising direction of corrosion protection of pump-compressor pipes, which is rapidly developing abroad, is the use of protective duplex systems, which are two-layer metallization and polymer coatings that have a synergistic protective effect.

Thus, complex studies have shown that in oil and gas fields with a high content of chlorides in formation water, it is economically feasible to use oil and gas pipelines made of low-alloy steels of the 06Cr1 type and diffusion-galvanizaned pump-compressor pipes; in deposits with an increased content of carbon dioxide, it is promising to use high-strength pump-compressor pipes made of martensitic steel 20Cr13 and ferritic-austenitic (duplex) steels of the type 02Cr22Ni5NMo3, and for deposits with an increased content of carbon dioxide and hydrogen sulfide – tubing made of an austenitic chrome-nickel-molybdenum alloy of the type 03Cr25Ni30Mo3Nb.

Conclusions

On the basis of complex physical and chemical studies of pipes of the oil and gas range of increased corrosion resistance from low-alloyed and high-alloyed steels, manufactured according to the developed technologies, recommendations were given for their rational use in oil and gas fields with different aggressiveness of reservoir waters.

The results of the work and recommendations for the rational use of oil and gas pipes with increased corrosion resistance can be used to increase the economic efficiency of production in the oil and gas industry.

References:


