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Influence of long-term operation on the properties of main gas pipeline steels. A review

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Underground pipelines during operation are affected by mechanical and corrosive factors. The susceptibility of cathodically protected pipe to hydrogen degradation increases, which contributes to stress-corrosion cracking. It is believed that the main factor in pipeline steels degradation is deformation aging, which increases strength and reduces plasticity. Volume microdamages also develop in long-time exploited steels. But in many cases, the base metal and welded joints of long-term operated pipelines retain satisfactory performance. Due to the high value of viscosity and plasticity of the metal in an as-received state, the metal state of long-term operated gas pipelines can be considered satisfactory.

Key words: long term operated pipeline, pipe steel, mechanical properties, stress-corrosion cracking, hydrogen embrittlement, cathodic protection.

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Introduction

Underground gas pipelines in Ukraine were built in the 70-80 s of the twentieth century, and today their service period is 40 to 50 years. During operation under comprehensive corrosion protection, they are exposed to mechanical and corrosive factors. Such factors are, for example, the corrosive action of the external environment (from the soil in case of damage to the protective coating) and the internal environment (corrosive effect of gas condensate) [1]. The absorption of hydrogen by pipe steel can lead to a decrease in plasticity, especially in the presence of concentrations of tension, and make them susceptible to the expansion of cracks under static loads. The load level and frequency of cycles, microstructure, chemical composition, and presence of welded seams, as well as the pressure and composition of gas and its temperature, affect the hydrogen thickening of steel. The characteristics of gas pipelines cause the emergence of static (from the pressure of the transported gas) and cyclical (due to temperature fluctuations) tensions of the two-axis tension-deformed state with different ratio rings and longitudinal components, variable tensions, etc. Due to fluctuations in gas pressure and voltage in the pipeline, cracks can form and develop in the presence of hydrogen (even at relatively low partial pressures of gas-like hydrogen). The combined action of these factors will likely lead to a change in the physical and mechanical properties of the metal.

When designing, the complex of properties is chosen in such a way that during construction and long-term operation, even under adverse conditions, the object could retain the specified indicators at the established level and withstand the influence of external factors during operation. Modern ideas on the impact of long-term operation on the metal properties of pipes are mainly based on the results of the study of operated pipes of normalized and hot-coated steels [1-5]. The results of such studies, despite some differences, indicate the tendency of pipe steels to deformation aging, which under certain conditions can lead to a change in the service characteristics of metal pipelines.

I. Theoretical foundations of the effect of hydrogen on steel degradation

The presence of hydrogen in an environment leads to deterioration of the mechanical properties of steels during plastic deformation (during stretch tests or under constant applied load). Particularly noticeable, this type of damage occurs in ferrite steels [3]. Due to the release of hydrogen from the working environment initiated by corrosion reactions and/or cathodic protection, many steel structures suffer rejection. Hydrogen induced breaking occurs in conditions of tension, leading to hydrogen brittle. Usually this manifests itself in the form of individual induced cracks, such as hydrogen scattering, hydrogen spattering parallel to the direction of load, and sulfide corrosion cracking.

Corrosion is a degradation of metal under the influence of the environment. This refers to an electrochemical process that involves the release of electrons due to the dissolution of the metal in the anodic area and the subsequent transition of the electrons to the cathode areas, where oxygen-saturated water is reduced to hydroxide ions. The main processes of recovery-oxidation involved in the corrosion process are represented by two half-reactions:

Anodic reaction (solution of iron)

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (1)$$

Cathodic reaction (recovery of hydrogen):

$$2H^+ + 2e^- \rightarrow H_2, \quad (2)$$

or reduction of oxygen in a neutral or alkaline solution

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-, \quad (3)$$

reduction of oxygen in acidic solution

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O. \quad (4)$$

Corrosion reaction:

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2. \quad (5)$$

During the corrosion process (1)-(5) the secreted atomic hydrogen recombines and forms molecules according to reactions (2) and (5) on the steel surface, which either are removed from the surface, or migrate into steel, where they recombine on structural defects:

$$H^+ + e^- \rightarrow H_{ads} \quad (6)$$

$$H_{ads} + H_{ads} \rightarrow H_2. \quad (7)$$

The protective coatings of the pipelines do not fully protect against the formation of hydrogen bubbles, especially in areas where the cathode potential does not reach the surface. This process, known as cathode disbandment, contributes to the interaction between pipeline coatings and OH-ions formed during water recovery. At a high cathodic potential, hydrogen penetrates through the edge of the defect to the wall of the pipe. The high focal resistance of the coating inhibits the penetration of cathode current under the coating to steel [7]. For cathodically protected pipe steel, susceptibility to hydrogen degradation increases [6, 7].

The relationship between hydrogen exposure and material characteristics such as microstructure, chemical composition, and mechanical properties is complex [3], so studies focused on hydrogen cracking of steels often lead to contradictory conclusions. The penetration of hydrogen is strongly influenced by the surface properties created during the processing of steel, namely: structural defects, micro-structural phases, inclusion, etc. The degradation of the pipe steel caused by hydrogen depends heavily on the crystalline lattice. Pipe steel microstructures consist of fragments that are potential traps for hydrogen. These locations of capture include dislocations, grain boundaries, alloy elements, defects, and grain boundaries. Hydrogen atoms migration into the steel structure and its attraction to the defects of the crystalline (grain borders, dislocations, vacancies, inclusions, phase separations) is the main condition of hydrogen induced degradation [3].

Hydrogen location inside the crystalline grid, where these atoms are less likely to pass through it without a strong delay, are considered irreversible places of capture (e.g., boundaries of the inclusion section). These sites have a high potential energy barrier that needs to be overcome to enable hydrogen atoms to get out of them. For example, irreversible hydrogen traps, such as the boundaries of martensite grains and mixed dislocation cores, typically have the energy of connection in the range of 61.3 to 62.2 kJ/mol. The energy of binding the hydrogen trap through the grain boundaries with strong disorientation and unsolved carbides is from 89.1 to 89.9 kJ/mol [8]. It is believed that hydrogen atoms, when irreversibly captured, do not diffuse through steel. On the contrary, atomic hydrogen captured by low-energy sites (e.g., dislocations and grain boundaries) is considered to be reversed. In cold-coated pipe steel, the authors [9, 10] revealed the presence of reverse hydrogen traps due to plastic deformation during manufacture. Cracks are initiated in a sensitive material under the complex influence of hydrogen and critical load levels, leading to hydrogen embrittlement. This idea is widely accepted, but today, the exact mechanism of hydrogen cracking is still the subject of intense discussion.

In the work [11] it is stated that in steel X70, micro cracks are formed at the boundaries of the "inclusion-matrix". A model was built to predict the quantitative dependence of hydrogen-induced destruction from non-metallic inclusions [11].

II. Methodical approaches to assessing the influence of long-term exploitation on steel properties

It is likely that the above degradation mechanisms are implemented in steels with prolonged operation. Consider methodological approaches to the study of such steels.

According to the tests to the method of artificial deformation aging of steel X52 (according to GOST 7268) received a significant increase in the ratio σ_{ys}/σ_{US} (σ_{ys} – yield stress, σ_{US} – ultimate stress) above the limit level, according to GOST 31447 and a slight embrittlement of the metal, manifested by an insignificant decrease in relative narrowing and impact viscosity. This indicates certain limitations of its application due to the strong deformation reinforcement of steel, which is not achieved under real conditions of pipe operation. A new method of modeling the operation degradation of pipe steels is proposed, which consists in electrolytic hydrogenation of specimens, loading by certain plastic deformation, and heating at 250°C [12-14]. The characteristics of pipe steels of varying strengths, 17G1S (analogue X52), X60 and X70 were compared with their properties after operational and laboratory degradation. The change in mechanical properties was estimated by the coefficient λ:

$$\lambda = 100\% \cdot (P_{expl} - P_{as\text{-}rec})/P_{as\text{-}rec}, \qquad (8)$$

where P_{expl} and $P_{as\text{-}rec}$ – characteristics of steels in operating and as-received conditions.

A slight increase in strength indicators σ_{US} and σ_{YS} for all operated steels and a noticeable decrease in plasticity indicators δ and ψ for steels X60 and 17G1S were detected. For 17G1S steel, both plasticity characteristics changed the most: δ decreased by 22% and ψ – by 18%, and for X70 there was no noticeable change in plasticity.

Deep micro-layers detected in the central part of the breaking surfaces for exploited steels were considered as signs of diffuse damage of the metal caused by the texture and hydrogen absorbed by metal. A comparison of results of stress-corrosion cracking tests showed that the characteristics of the X52 and X60 steels in their original states in the corrosive environment vary very slightly [13].

At the same time, artificially degraded steels are characterized by increased sensitivity to corrosive cracking. As fractographically shown [13], a scattering along the boundaries of the separation of the grains of ferrite and perlite with the formation of deep secondary intergranular cracks, and the layering of ferrite and cementite inside the grain of perlite. The destruction according to this mechanism was detected near the outer surface of the specimens and in the central part of the surfaces of the laboratory-degraded specimens, which, according to the authors opinion, indicates the key role of hydrogen during cracking process.

For the quantitative characteristics of pipe steels embrittlement after their long term operation, the concept of mechanical stability (a complex of strength and plasticity characteristics that prevent fragile destruction of a structure element in the given conditions of operation) is applied to structure materials based on physical nature parameters of materials breaking [15]. Mechanical resistance is described by parameters K_{ms}, K_{msc}, P_{ms}:

$$K_{ms} = \frac{R_x}{\sigma_2} = \frac{R_x}{\sigma_{0,2} \times 10^n}, \qquad (9)$$

Where K_{ms} – the coefficient of mechanical stability; R_x – brittle strength (resistance to the microchip P_{ms}: for structural steels), namely the breaking stress of specimen at a certain (critical) level of deformation $\delta_c \approx 2\%$; σ_2 – the strength of the metal, deformed to $\delta_c \approx 2\%$, n – the reinforcement indicator by Holloman [16].

The concept of mechanical stability is based on the assessment of the critical coefficient K_{ms}, which characterizes the loss of mechanical stability due to brittle factor action.

$$K_{msc} = \frac{R_x}{\sigma_{2C}}, \qquad (10)$$

where σ_{2C} – the brittle strength of the specimen under embrittlement factor action (stress concentrator) at a critical temperature of brittle transformation. The K_{msc} index reflects the susceptibility of the metal to brittle destruction and allows to determine the parameter P_{ms} as follows:

$$P_{ms} = \frac{K_{ms}}{K_{msc}} = \frac{\sigma_{2C}}{\sigma_2} \qquad (11)$$

where P_{ms} – the indicator of the residual mechanical stability of the specimen under the action of the embrittlement factor. This parameter characterizes the mechanical stability reserve, in the presence of which no brittle destruction is expected during the action of additional embrittlement factors.

When it is not possible to determine the characteristics of the brittle strength R_x (P_{ms}) experimentally, it can be calculated by the methodology given in [19] using the basic mechanical properties of the metal σ_{ys} and σ_{US} and the relative narrowing ψ.

The concept of mechanical stability is based on the use of relative narrowing ψ (along with other plasticity characteristics). The authors [15] believe that the relative narrowing better reflects the degradation of gas pipelines steels, since the disclosure of dispersed defects can affect the relative lengthening and thus lead to its increase [15, 17]. The trend of changing the relative narrowing ψ for the steel under investigation over the time of its operation τ corresponds to the general notion of a partial loss of plasticity during long-term operation.

Simultaneous deterioration of strength and plasticity characteristics is a feature of operational degradation of pipe steels caused by the development of dispersed damage in the metal wall volume of the pipe. In this case, the strength characteristics and relative extension are not sufficient to analyze the state of the metal, as they formally indicate that in the process of long-term operation, the metal will undergo plastification. Thus, the residual mechanical resistance of the specimen under the action of the thickening factor most accurately reflects the change in the characteristics of the metal during operation.

For oil and gas pipelines steels the regulatory documents set requirements for impact viscosity. However, corrosion resistance, which is an important characteristic of structural integrity assessment, is not regulated. The authors [18] developed a method of assessing the operational degradation of pipe steels, that proposes to determine and regulate the minimum permissible value of the corrosion crack resistance characteristics, in particular, the threshold of the stress intensity coefficient based on the J-integral for stress-corrosion cracking, Jscc. This method is based on the modification of the regulated limit values of impact viscosity separately for the metal in as-received conditions and the exploited metal, taking into account the increased susceptibility of steel to stress-corrosion cracking. The method is applied to assess the operational degradation of pipe steels of strength class X52 with ferrit-pellite structure [18]. The boundary lines were considered as conservative dependencies of impact viscosity KCV = f(τ) and the J-integral threshold based on the Jscc = f(τ) stress intensity coefficient of the pipe steels in dependence with operation time τ. The threshold value of J-integral J_{scc} steels was determined in the NS4 solution modeling the soil environment. The impact viscosity of steels in as-received state (~100–300 J/cm^2), at least twice more than the minimum permissible value (50 J/ cm^2). At the same time, the impact viscosity of the exploited steel is sometimes lower than the normalized. This reduction in resistance to brittle destruction occurs after 20-25 years of operation [20]. The standard values are given in B&R 2.05.06.

The effectiveness of mechanical, structural-fractographic, and electrochemical methods for assessing the operational degradation of pipe steels, taking into account the corrosive-hydrogen impact of aggressive media was analyzed in [19]. It was found that preliminary hydrogenation increases the sensitivity of mechanical methods by increasing the susceptibility of degraded steels to hydrogen cracking. Among the structural factors, the influence of the texture of the lease is distinguished, among the fractographic factors, the contribution of the fraction of low-energy destruction, in particular layering and intracellular decomposition, is noted. The method of microfractographic analysis determines the contribution of flooding to the development of steel microdamage. Electrochemical methods allow to the prediction of steel resistance to fragile destruction by changes in polarization resistance and surface destruction potential. It is also possible to assess the degree of diffuse damage and the susceptibility of steel to scratching with the participation of hydrogen. As part of the concept of physical mechanics, the dynamic destruction of 17G1S steel specimens is represented as a sequential process of loss of resistance to shift that occurs at different structural/scale levels of the material. The characteristic stages for different destruction modes have been analyzed, as well as typical load levels and fluctuation periods.

The efficiency of mechanical, structural-fractographic and electrochemical methods for evaluating the operational degradation of tube steels taking into account the corrosion-hydrogen influence of aggressive media is analyzed in the work [19]. It has been established that the preliminary hydrogenation increases the sensitivity of mechanical methods by increasing the susceptibility of degraded steels to hydrogen cracking. Among the structural factors, the influence of the texture of the lease is distinguished, among the fractographic factors, the contribution of the fraction of low-energy destruction, in particular layering and intracellular decomposition, is noted. The method of microfractographic analysis determines the contribution of flooding to the development of steel microdamage. Electrochemical methods allow to the prediction of steel resistance to fragile destruction by changes in polarization resistance and surface destruction potential. It is also possible to assess the degree of diffuse damage and the susceptibility of steel to scratching with the participation of hydrogen. As part of the concept of physical mechanics, the dynamic destruction of 17G1S steel specimens is represented as a sequential process of loss of resistance to shift that occurs at different structural/scale levels of the material. The characteristic stages for different destruction modes have been analyzed, as well as typical load levels and fluctuation periods.

To assess the degree of operational degradation of gas pipeline steels, it is proposed to use true deformation diagrams [20, 21]. It is shown that the influence of the absorbed hydrogen of the 17MnSi steel during the long-term operation is manifested through the growth of micro-defects in the wall of the gas pipeline (in the form of dispersed damages) and a decrease in the resistance of steel to brittle destruction. The obtained results demonstrate the advantage of using true strain dependencies instead of nominal.

The harmful effects of hydrogen on the mechanical properties of microlalloyed X70 steel were assessed using static tensile tests of smooth specimens and flat specimens with a central hole, as well as Sharpe impact resistance tests [22]. The hydrogen induced changes in the behavior of fatigue crack development are also investigated. Testing was carried out on specimens that were aged for 4 years, and on specimens that after four years of aging were electrolytically charged with hydrogen. It is found that the size of the plastic zone at the top of the growing fatigue crack, which develops on the surface of the surface of the hydrogenated specimens, is much greater than that of not hydrogenated.

The authors found [23] that hydrogen atoms are easily separated at the ferrite/pearlite interface without external loads. During rapid deformation, hydrogen penetrates into pearlite and interacts with its internal vacancies, which leads to transverse fracture that starts from pearlite. Under slow deformation, the ferrite/pearlite interface is more vulnerable to hydrogen degradation, leading to intergranular cracks and an increased tendency for secondary cracks to form.

III. Review of experimental data on steels degradation under the influence of hydrogen

In a number of works of specialists of H.V. Karpenko Physical and mechanical institute of the National Academy of Sciences of Ukraine the research results of mechanical and corrosive properties degradation of domestic steel 17G1S and foreign production X52 after long term operation of main gas pipeline for 28-40 years are presented [24, 25]. It is noted that the transported product not only causes corrosive damage to the inner surfaces of pipelines and oil storage tanks, but also becomes a source of metal hydrogenation, so that steel degrades under the combined action of mechanical stress and hydrogen [28]. Corrosion of the inner surface of the pipe is the most intense in its lower part due to the action of residual water, which is separated from the oil product. The exploited steel in the lower part of the pipe, compared to the initial state, is substantially micro-damaged (the defects in metal are hydrogen traps and, accordingly, affect the hydrogen desorption kinetics when assessing its permeability through the steel), which can be associated with the compatible action of the absorbed hydrogen metal and the long-term load. Operational degradation of metal, including welded joint, is confirmed by a sharp decrease in impact strength. At the same time, it was proposed that the material should be compared not only in the initial and exploited states, but also on specimens from the upper and lower parts of the pipe. In particular, steel in as-received state has the highest impact strength (180 J/cm^2), and the impact strength of specimens made of the area "top" part of the operated pipe is twice smaller (95 J/cm^2). During the determination of the impact viscosity of the "bottom" area of pipe, the destruction occurs along the tangent line of pipe (along the disbonding fibers), typical for industrial pipelines of oil transportation and caused by the pressure of the diffusive-moving atomic hydrogen recombined into a molecular form (so-called blistering). Thus, the examination of main oil pipelines only for the presence of surface defects and corrosion thinning of the pipe wall may be insufficient to justify their workability due to a significant decrease in the resistance to brittle cracking and high sensitivity to hydrogen brittleness. This is evidenced by the deterioration of the mechanical properties of the parts of the pipe or tank that have been in contact with the transported medium during operation and is manifested in the embrittlement of the metal (reduction of ductility and resistance to destruction) and changing the electrochemical parameters. But the oil pipelines are not the subject of our review.

The main factor of pipeline steels degradation is their deformation aging, which increases strength and reduces plasticity and impact viscosity (stage I). However, if the operation duration approaches to 20 – 30 years, volume damages develops in the metal, which determines a number of features in the mechanical behavior of the material (stage II). Long-term operation at the stage of II eliminates the strengthening of the material by deformation aging, so you can observe even a simultaneous decrease, on the one hand, strength and hardness, and on the other hand – decrease the resistance to brittle cracking. Another feature lies in the different nature of the varying characteristics of plasticity of exploited steels: decrease of ψ and increase of δ [28].

It is proposed to distinguish the degradation of the surfaces of the pipeline (damage under the influence of mechanical, corrosion and other factors) and degradation of the material "in volume" (deterioration of properties, if not the entire volume of the metal, then commensurate with the characteristic size of the pipe - for example, wall thickness or a certain part of the pipe) [26, 27]. The cause can be both structural and deformation changes (deformation aging), and the development of scattered damage. The gas transported by main pipelines is considered as a corrosive non-corrosive medium in general, but under real operating conditions, due to fluctuations in gas temperature and the environment, it is possible to delay the gas condensate on the inner surface, and the salts, organic and sulfur-containing substances present in it, CO_2 can initiate internal corrosion. This medium can interact electrochemically with the metal with the release of hydrogen and accelerate the degradation of the physical and mechanical properties of steel with the combined action of mechanical stress and hydrogen.

Long-term operation of gas pipelines causes a slight decrease in hardness, strength limit, conditional yield limit and a noticeable increase in the relative elongation of low-alloyed manganese and silicon steels, as well as reduces the anisotropy of the properties acquired in the process of manufacturing pipes [28, 29]. The corrosion potential of the exploited steel up to 20 – 30 mV is more negative than the metal potential of the reserve pipes, and the corrosion current is slightly higher.

One of the consequences of degradation after 40 years of operation in the works [30, 31] is an example of the macrostratification of the elbow section of the gas pipeline with the release of a crack-like defect on the surface of the pipe and it is concluded that the stratification of metal is due to the joint influence of workloads and hydrogen absorbed by metal during long-term operation. Impact strength is defined on short cross-section specimens, the fracture plane in which parallel to the bundle plane [32]. The conclusion regarding degradation is confirmed by abnormal parameters of wall thickness and a decrease in the hardness and ductility of the bent part of the pipe. But in our opinion since this section of the gas pipeline was cold bended and exploited in atmospheric conditions, it is quite natural that the possibility of delamination during this process, especially since there is no data on the properties of the section for operation.

17G1S steel (X52 strength category steel) has the lowest corrosion resistance in NS4 solution and the resistance of X70 steel both in as-received state and after long-term operation was the highest [32]. But the degree of corrosion degradation due to long-term operation was the highest for X70 steel. For the exploited steels, the increase in intensity of cathode and anode processes is noted, which is manifested in the increase of the corrosion current density, reduction of the polarization resistance and displacement of the corrosion potential to more negative values. In our opinion this is a rather controversial point of view: electrochemical parameters are determined by the chemical composition of steel and are studied on the ground surface, and the chemical composition after long operation does not change, so their significant change is unlikely.

In work [33] also confirmed a reduction of plasticity characteristics and increase of strength characteristics due to operational degradation, and the higher level of strength of steel in the initial state, the less changing its characteristics. So, the ductility of steel X70 has not changed, and the steels 17G1S and X60 have decreased. These effects are due to the structural features of the steels. Indeed, the texture of both axial and diametrical cross-section of pipes from these steels is revealed: the length of almost continuous rows of perlite grains in the axial direction reached 500 microns, and in the transverse 40 microns. The damage between the ferrite and perlite grains along and across the rolling direction was hydrogen traps and prevented its diffusion redistribution in the cross section of the pipes. Accumulated in the traps hydrogen contributed to stratification along the boundaries of the section and contributed to the localization of deformations in the most weakened areas. Fractographically revealed signs of operational degradation of steels of different strength: first, it is a textured nature of the destruction of specimens at the macro level in the form of bundles in the direction of the pipe rental, which are caused by operational damage to steels. It is assumed that they were led by hydrogen absorbed by the metal during long-term operation and accumulated in defects along the boundaries of the section. Secondly, in the central part of the cracks of the form I, large and flat lenticular areas with small pits are found, accumulating hydrogen on the bottom, which contributed to the destruction of partitions between them. Thirdly, within the conic sections of the fracture of all the studied steels in the mode of displacement, there are small parabolic pits, large flat pits with a characteristic relief of parallel traces of the slope of the sliding strips to their surface. It is assumed that this indicates their existence in the cut of specimens before the tensile test. These structural-fractographic features of degradation are inherent in all steels, most of all – 17G1S steels, the strengthening of which was accompanied by a greater decrease in ductility due to degradation.

Deterioration of the properties of metal of long-term operated main gas pipeline was revealed by the authors [36] by a drop in impact viscosity, a decrease in relative narrowing, and an increase in hardness; the plasticity parameters of the metal changed in the opposite way. This is explained by the intensive development of defects at the micro- and sub-micro levels during long-term operation, which is confirmed by fractographic analysis.

The regularities of the effect of scattered damage on metal deformation processes of a main gas pipeline operated for 40 years at different scale levels are summarized using the approaches of physical mesomechanics [36].

Deformation process of the damaged material was analyzed using strain-stress curves, the separate sections of which correspond to destruction stages. The established regularities are proposed to be used to assess the resistance of the main gas pipeline to fatigue damage and rational selection of the permissible stress value taking into account stress concentrators [37].

Diagnostics of the current state of the main gas pipeline after 33 years of operation revealed not only operational but also welded joint defects that occurred during the construction phase [38]. For example, a welded joint crack that originated during operation from technological microdefects during welding. A weld overheating area with coarse grains and weakened boundaries was found near the crack initiation site, which contributed to the formation of delaminations during the cracking process. Small micropores in the crack development zone may indicate the influence of hydrogen on the weld metal. It is likely that the crack originated in the coarse grain zone, and additional factors contributing to the formation of the macro defect were numerous micropores with a diameter of several micrometers and cracks oriented along the grain boundary. The cracks formed in the weld zone under the influence of damage accumulated along the grain boundaries. This damage occurred in the first hours after welding, but it was scattered and did not manifest itself for a long time, as the level of welding stresses was insufficient for its growth. Under the influence of operational factors, microdefects grew and merged. Such a technological effect may be the "superposition and summation" of welding and process stresses, which leads to the localization of microdeformation processes. An additional effect may be the influence of weld watering. Thus, from the damage analysis, it can be concluded that the defect was formed as a result of unfavorable structural and mechanical factors: austenitic grain size, a significant gradient of the grain structure in the weld zone, and grain compaction.

The degree of susceptibility to hydrogen embrittlement of X70 steel in a mixture of natural gas and hydrogen (0.1, 0.5, 1, 3, and 5 vol. % hydrogen) increases with increasing hydrogen concentration in the mixture [39]. The conditions of the hydrogen gas mixture do not significantly affect the load and flow in the elastic region, while the maximum load decreases significantly with increasing hydrogen concentration. By evaluating the absorption energy of the specimens as a function of the saturated hydrogen pressure, the plastic-brittle transition was determined. The degree of degradation of the strength of mechanical properties of pipe steel X70 is not affected by the time of its exposure to gaseous hydrogen.

Under the synergistic effect of hydrogen and stress concentration, the degree of plasticity degradation of X70 steel increases with an increase in the stress intensity factor K_t, and with an increase in the partial pressure of hydrogen in the mixtures, the effect of K_t on hydrogen-induced degradation increases [40]. At the crack tip of the specimen, the hydrogen concentration is maximal and increases with increasing K_t, which is assumed to be one of the reasons for the severe hydrogen embrittlement of specimens with a large K_t. As the axial stretching of the specimens increases, the maximum hydrogen concentration at the tip of the cut begins to dominate the amount of hydrogen in the normal lattice regions and, subsequently, in the trapped regions.

Based on the studies conducted by the authors of [40], it was found that in many cases, the pipeline material (base metal and welded joints) retains high performance after long-term operation. The most noticeable changes in the physical and mechanical properties of the material due to operational influences can occur in localized areas where defects, stress concentrators, deformed zones, etc. are located.

A series of studies by the E.O. Paton Electric Welding Institute [41-43] evaluated the deformation aging of metal pipes made of controlled-rolled steel with diameters of 1220 and 720 mm from X70, 10G2BT, 10G2T, 13GS steels after long-term operation and after storage for 2 to 21 years (which excluded the influence of additional cold plastic deformations during the manufacture and operation of the pipes). Pipes made of X70 steel after 21 years of operation were cut from the section of the pipeline through the beam with a reservoir.

The studied materials are typical pipe steels, micromanganese, vanadium (X70), nickel and titanium (10G2BT), titanium (10G2T, 13GS). The pipe material of 13GS steel, compared to other steels, has lower strength indicators, including the ratio σ_{YS}/σ_{US}.

For the emergency stock pipe specimens, no deviations of service characteristics were detected from the controlled spoilage rate after storage ((σ_{US}, σ_{YS}, δ_5, σ_Y/σ_{US}, impact toughness) of the base metal and welded joints from the normative requirements and, accordingly, a noticeable change in the state of the material of the tubes as a result of the natural state (Figure 1). Only for the

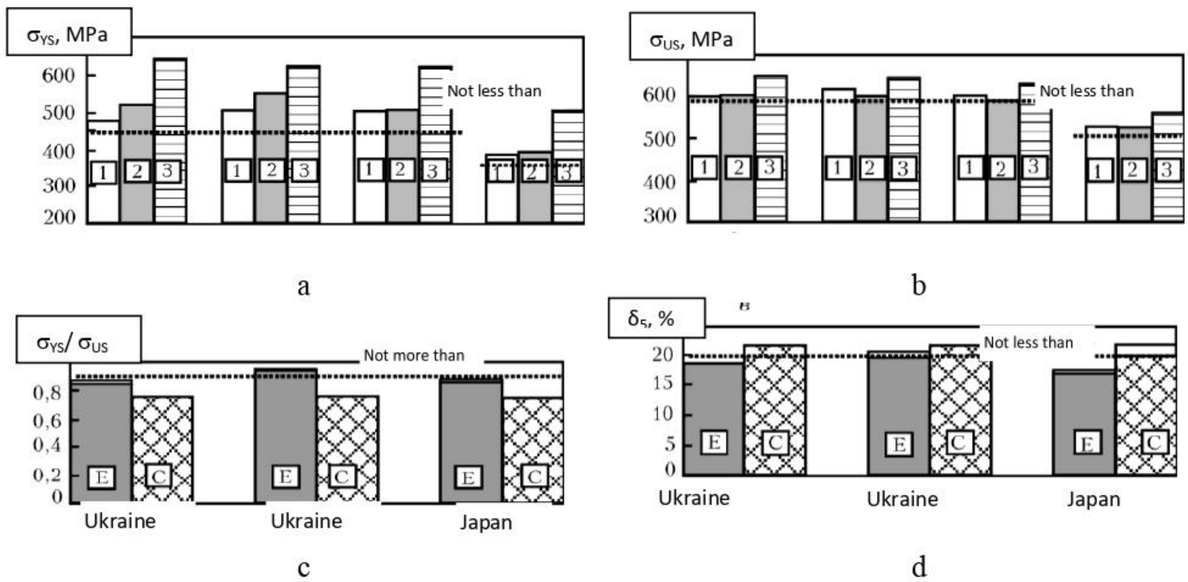

Fig. 1. Mechanical properties of the metal of the stockpipe specimens: 1 – in the initial state; 2 – after aging (heating to 250°C); 3 – after aging with preliminary deformation (2 %); e – pipes after long-term exploitation; c – certificate data; dotted line – normalized value according to B&R 2.05.06.

10G2T steel was there a slight change in the strength characteristics compared to the data of the pipe certificates [44].

However, it was found that when heated to 250°C for 1 year, which is used to activate the pre-aging process (Figure 1), the metal properties of pipes from different steels do not change equally, which is probably due to the influence of the metal-phase factor. Thus, for 13GS steel, the aging process is accompanied only by a change in the characteristic of the deflection of the specimens at the yielding stage (increase in the yielding area) without any noticeable effect on the strength. In other steels, such as X70, σ_{YS} and σ_{YS}/σ_{US} are being upgraded. The effect of aging is caused by an increase in the critical embrittlement temperature to -20°C.

After additional cold deformation, even at low values of deformation, and the next stage, a significant change in the service characteristics of the material is expected for all the studied pipes and in some cases deviations from the normal requirements (Figure 1).

Thus, after 2 % of cold plastic deformation and the next stage, σ_{YS} ($\Delta\sigma_{YS}$ to 164 MPa), σ_{US} ($\Delta\sigma_{US}$ to 59 MPa) and, respectively, σ_{YS}/σ_{US} ($\Delta\sigma_{YS}/\sigma_{US}$ to 0.16) increase. In addition, flatness is noticeably decreasing ($\Delta\delta_5$ by about 7%). In the current state, the value of σ_{YS}/σ_{US} in X70 and 10G2T steel products reaches 0.96-0.98, which does not meet the established requirement (no more than 0.9). In the last article 10G2BT, the fluidity limit is practically at the level of temporary resistance to development and, accordingly, σ_{YS}/σ_{US} is close to one – 0.99. As the ratio of σ_{YS}/σ_{US} grows to almost 1 after the degree, which is observed in countries with high initial values of this indicator (more than 0.8), a significant reduce in the level of plasticity is expected. The resistance to brittle destruction of operated steel at the stage of development of a viscous crack also decreases markedly [41].

The sensitivity to ageing of the metal of the X70 steel pipe, which is used in complex conditions, was confirmed by the study of specimens of pipe cut from the gas supply in the area before passing through the beam. The strengthening (increase σ_{YS}) and decrease in the plasticity ($\Delta\delta_5$) of the main metal was detected (Figure 2). For example, in one of the specimens from X70 steel, we observed an increase in yield strength from 456 to 596 MPa, tensile strength from 598 to 634 MPa, and σ_{YS}/σ_{US} ratio from 0.76 to 0.96 (versus 0.9 as required). The relative extension of δ_5 decreased from 22 to 18%, which is below the established norm. Thus, according to some indicators of mechanical properties, the material of X70 steel pipes after prolonged exposure does not meet the requirements of regulatory documents [44].

At the same time, due to the high viscosity and plasticity of the material in as-received state, the state of the hardened metal of the investigated pipes (after exploitation) can be considered satisfactory. The fiber content in the break surface of the specimen is 100 % up to a test temperature of -30°C. The impact toughness of the main material of the pipes after exposure (Figure 3) has high values in a wide temperature range, and at a temperature of 0°C it is several times higher than the normative value (not less than 78.2 J/m^2) [42, 44].

Viscous-laminated fracture appearance with disintegration of the original specimens (which occurs in the temperature range from 20 to -80°C), the temperature of brittleness is -100°C and below) of the metal specimens after exposure did not differ from the corresponding characteristics of the metal specimens of the emergency stock and are typical for the X70 steel of the controlled rolling.

In the welded joints from micro-alloyed controlled-rolling pipes, the level of the impact toughness depends on the breaking area of the impact specimens. Due to the structural changes of the steel under welding, the viscosity

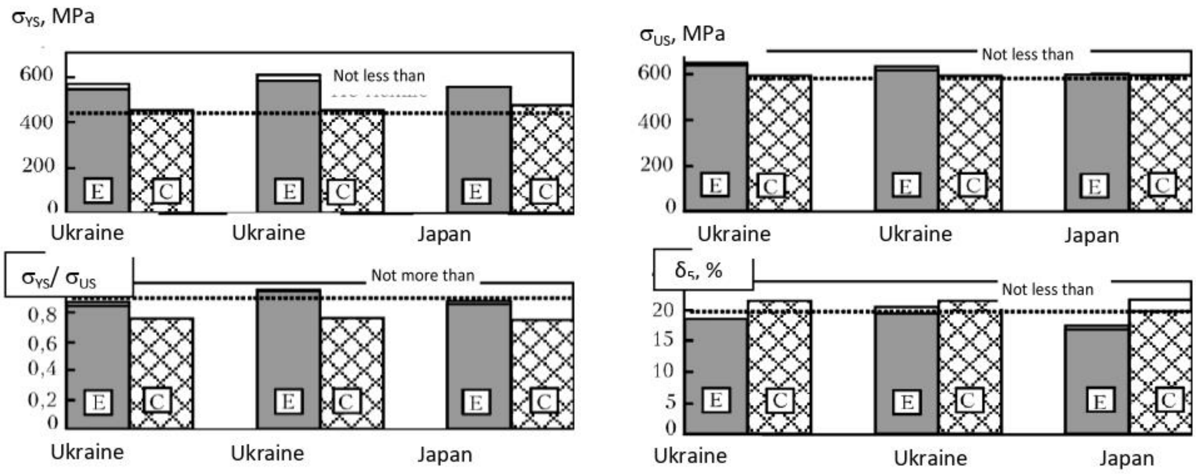

Fig.2. Mechanical properties of the material of gas pipes with a diameter of 1220 mm made of X70 steel of controllable rolling of different manufacturers after exploitation: E – pipes after long-term exploitation; C – certificate data; dotted line – normalized value according to B&R 2.05.06 [44].

of certain zones of welded joint is decreased compared to the base metal, which is a common phenomenon for microalloyed steel pipes in the original state. Characteristic changes in properties in different parts of the welded joints were found in the pipes both after exposure and in the pipes of the emergency stock.

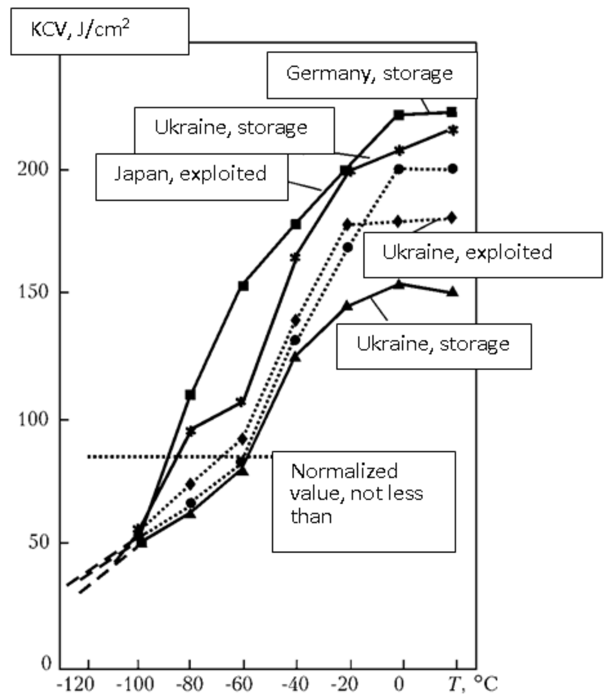

Fig. 3. Impact toughness of a 1220 mm diameter pipe made of X70 steel from various manufacturers [44].

No noticeable changes in the service life characteristics of the metal of the welded joints were detected in the studied pipes after the exploited loads. However, we should not exclude the possibility of changes in the state of the material, especially in the heat affected zone. The rates of deterioration of fine-grained areas of heat affected zone, where plastic definition can be localized, can be considered the same as for the main material.

Thus, after three years of exploitation loading in the foreground area through the gully, there was a strengthening as a result of the deformation ageing (increase in the values of σ_{YS} and the ratio of σ_{YS}/σ_{US}), as well as a decrease in the δ_5 of pipe metal. At the same time, in most cases, the indicators σ_{YS}/σ_{US}, δ_5 of the metal of the investigated pipes did not correspond the normative requirements for gas pipes. However, due to the high levels of impact toughness in the initial state, the hardened pipe metal is characterized by satisfactory resistance to destruction. The reaction and property of the metal as a result of its defragmentation depends on the state of the controlled test article in the initial state.

In connection with the negative effect of deformation ageing under the influence of long-term stress loading and additional cold plastic deformation (even at relatively low values of plastic deformation), the assessment of the current state of gas pipelines, made of high-strength pipes, will be of particular importance. Due to deformation ageing process the steel is further strengthened (with the initial values of $\sigma_{YS}/\sigma_{US} = 0.8$, this indicator rises to almost 1) with a corresponding change in the ductility resource.

The main problem of the performance of such a material is the reduction of resistance to viscous destruction and the associated increase in its sensitivity to stress and defects, increasing the susceptibility of the material to creating of destruction centers.

It should be expected that the most significant changes in the steel of the controlled rolling (as well as other types of pipes) will be observed in the areas of deformation damage (corrugations, dents, areas of maximum defamation when bent). Therefore, when diagnosing of existing main gas pipelines it is advisable at first to determine the location of the marked areas, the state of the metal, and the defects. In addition, the complex sections of the pipelines (passages through various obstacles, turns of the track, places of sagging in unstable grants), where additional forces are put on the pipe material must be investigated. Detection and elimination of dangerous defects in the areas is of primary importance for prolonging the service life of the deformed ageing material.

When determining the current state of the metal of the pies of existing main pipelines, it is advisable to focus on the indicators of service life characteristics of the metal, which are critical for the deframed state of the controlled rolling, namely σ_{US}, σ_Y/σ_{US}, δ_5. The residual values of the KCV should be checked in the pipes, the KCV of the metal of which according to the certificates was close to the minimum acceptable value in accordance with the established standards.

Conclusions

Underground main gas and oil pipelines, built in the 70-80s of the 20th century, and during operation under the conditions of comprehensive anti-corrosion protection, endure the influence of mechanical and corrosion factors. Protective coatings of pipelines do not fully protect against water penetration to the pipe wall, therefore, for the simultaneously protected pipe resistance to water degradation increases. Absorption remains aqueous, which is formed under cathodic polarization, can lead to a decrease in ductility and contribute to the expansion of stress corrosion cracking.

Deformation aging, which increases strength, reduces plasticity and impact toughness, is noted as the main factor in the degradation of main pipeline steels. If the duration of operation approaches 20 – 30 years, it is considered that damages develop in the volume of metal, due to the development of which there is a simultaneous decrease in strength and hardness, as well as resistance to brittle fracture. A change in the plasticity characteristics of the used steels was noted, with a decrease in relative narrowing and an increase in relative elongation. The corrosion potential of the used steel is 20 – 30 mV negatively than the potential of the metal of the stock pipes, and the corrosion current is somewhat higher.

It is proposed to distinguish the degradation of pipeline surfaces (damage under the influence of mechanical, corrosive and other factors) and the degradation of the material "in the volume" (deterioration of the properties of the metal commensurate with the characteristic dimensions of the pipe wall thickness or a certain part of the pipe). The reason can be both structural and deformational changes (deformation aging) and the development of scattered damage.

In many cases, the metal of pipelines (base metal and welded joints) retains high performance after long-term operation. The most noticeable changes in the physical and mechanical properties of the material due to operational influences can occur in local areas where defects, stress concentrators, deformed zones, etc. are located. According to some indicators of mechanical properties, the metal from such sections of pipeline steel does not correspond the requirements of regulatory documents. At the same time, due to the high value of the viscosity and plasticity of the source metal, the condition of the strengthened metal of the investigated types (after the application) can be considered satisfactory. The effective viscosity of base metal, for example, after exploitation, has high values in the typical temperature range, and at temperature of 0°C it is several times higher than the normed value (at least 78.2 J/ cm^2).

Presence of micro-layering of the surface after rupture of specimens of exploited steels is contradictory. Some authors claim that the viscous appearance of fractures with splits is typical for X70 steel and in the temperature range from 20 to -80°C, and is not recognizable for the metal of storage pipe. Others consider surface micro-delamination in fractured specimens of in-service steels as signs of diffuse damage to the metal caused by structure and absorbed hydrogen. It is also shown that the characteristics of corrosion cracking of X52 and X60 steels in their initial state in a corrosive environment change slightly, and artificially degraded steels are characterized by increased sensitivity to corrosion cracking.

A comparison of the characteristics of pipe steels X52, X60, and X70 with their properties after operational and laboratory degradation showed a slight increase in the strength indicators σ_{US} and σ_{YS} for all operated steels and a noticeable decrease in the plasticity indicators δ and ψ for steels X60 and X52, for X70 a noticeable change in plasticity characteristics not found These effects are caused by the structural features of steels. The steel of strength category X52 has the lowest corrosion resistance in NS4 solution, and steel X70 has the highest both in the as-received state and after long-term operation. But the degree of corrosion degradation after long-term operation is the highest for X70 steel. For exploited steels, an increase in the intensity of cathodic and anodic processes was noted, which is manifested in an increase in the corrosion current density, a decrease in polarization resistance, and a shift in the corrosion potential to more negative values.

It should be expected that the most significant changes in controllable rolling steel (as well as other types of standard steel) will occur in the zone of deformation damage (bents, dents, zones of maximum deformation, and bending). Therefore, during the diagnosis of the operated main pipelines, first of all, it is worth determining the condition of the specified areas, the metal surface, and the defects. In addition, the complex sections of the routes (passages through different obstacles, pipeline track turns, pipes sagging, etc.) where additional strain loads on pipes occur. When determining the current state of pipeline metal it is appropriate to pay attention to the indicators of plasticity of metal, which are critical for the deformation aging steel of controllable rolling, namely σ_{YS}, σ_{YS}/σ_{US}, δ_5. Residual values of the ultimate viscosity must be checked in pipes the ultimate viscosity of which according to the certificates close to the minimum acceptable according to the established norms values.

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Вплив тривалої експлуатації на властивості сталей магістральних газопроводів. Огляд

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Підземні трубопроводи в процесі експлуатації зазнають впливу механічних та корозійних чинників. Схильність катодно захищеної поверхні труби до водневої деградації підвищується, що сприяє розвитку корозійного розтріскування. Вважається, що основним чинником деградації трубних сталей є деформаційне старіння, яке підвищує міцність і знижує пластичність. Об'ємні мікропошкодження також розвиваються в тривалоексплуатованих сталях. Але основний метал і зварні з'єднання труб тривалоексплуатованих газопроводів зберігають задовільні експлуатаційні властивості завдяки високому запасу ударної в'язкості і пластичності металу у вихідному стані.

Ключові слова: тривало експлуатований трубопровід, трубна сталь, механічні властивості, корозійне розтріскування, водневе окрихчення, катодний захист.