ENVIRONMENTALLY ASSISTED DEGRADATION OF THE PHYSICAL AND MECHANICAL PROPERTIES OF LONG-TERM EXPLOITED STRUCTURAL STEELS

Hryhoriy Nykyforchyn

Karpenko Physico-Mechanical Institute of the National Academy of Sciences of Ukraine

Lviv, Ukraine

(e-mail: nykyfor@ipm.lviv.ua)

INTRODUCTION

Loss of integrity of long-term exploited structures is usually caused by the development of macrocracks, which is considered in the frame of fracture mechanics approaches. Therefore structural materials, including steels, are chosen on a stage of design with sufficient level of crack initiation and propagation resistance in operating conditions. However the main relevant physical and mechanical properties, which are taking into consideration on the stage of design, worsen often during the operation. Such in-bulk material degradation (degradation of properties) increases a risk of structure integrity loss.

The in-service degradation of mechanical, corrosion and corrosion-mechanical properties of structural steels operating in corrosive environments is considered in the paper under an angle of a role of corrosion-hydrogenated environments in the process of degradation. Investigations were carried out in the Department of Corrosion-Hydrogen Degradation and Materials Protection of Karpenko Physico-Mechanical Institute and based on a comparison of materials in as-received state and after service. Two types of steels are considered here: high temperature steels for power plants and steels for main oil and gas pipelines.

The problem of in-service material degradation has many topics. Besides of the general degradation laws following topics are important: susceptibility of material properties to the degradation, environmental effects on the in-bulk material degradation, degradation mechanisms, in-laboratory modelling of degradation, NDT of material degradation.

GENERAL DEGRADATION LAWS

In Figure 1 the general laws of in-service degradation mechanical properties of structural steels [1–8] are shown. Usually in-bulk degradation of steels operated at ambient temperature is related to with the process of deformation aging (the stage I). At elevated temperatures the degradation is caused by diffusion. On one hand the stage of deformation aging causes an increase of the strength and hardness. On the other hand it results in decrease of plasticity and the brittle fracture toughness.

The stage II is the stage of dissipated damaging, which is more dangerous in respect to the loss of integrity. At the high level it is accompanied by worse mechanical behaviour of metal: a) decreased strength and hardness as well as reduced brittle fracture toughness; b) increased elongation at a decrease cross-section area; c) the deflection from the straight line on stress-strain curve may be caused not by the beginning of macroplastic deformation but due the compliance increase caused by dissipated damaging.

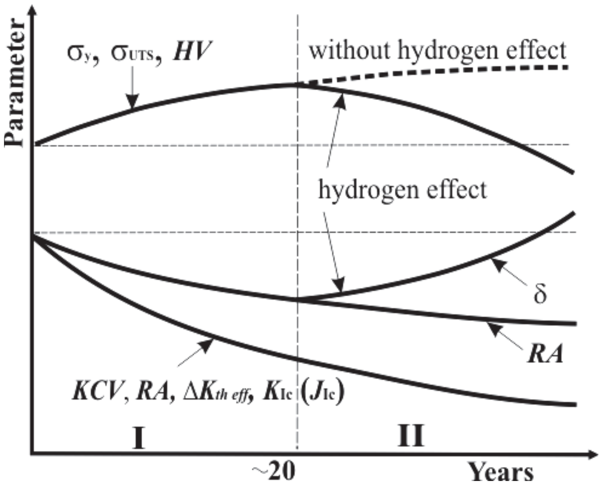

Fig.1 Two principal stages of in-bulk material degradation: I – stage of deformation aging; II – stage of dissipated damaging.

SUSCEPTIBILITY OF THE MECHANICAL PROPERTIES TO IN-SERVICE DEGRADATION

The most important result of the in-service material degradation is a reduction of brittle fracture toughness. Therefore test conditions that cause embrittlement provide a better comparison of relevant mechanical properties of steels in as-received state vs. after service state. These are tests of specimens with notches or cracks, under impact loading, at low temperatures, in corrosion environments either after preliminary hydrogenation or during the hydrogenation. Figure 2 shows the change of the brittle fracture resistance with the operation time.

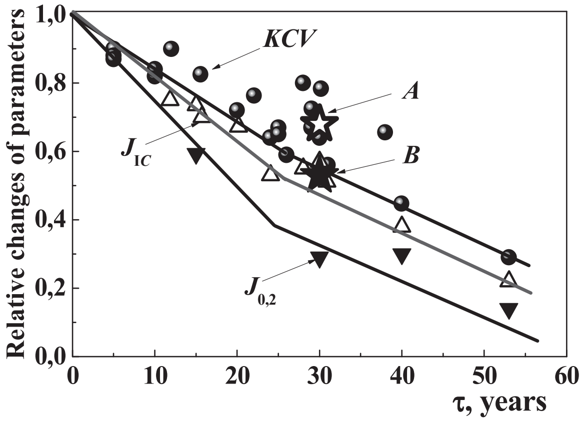

Fig. 2 Effect of service time on the characteristics *KCV*, J_{Ic} (corresponded to a start of preliminary crack), $J_{0,2}$ (crack growth 0,2 mm) of the main oil and gas pipeline steels 14KhGS (0.14C-Cr-Mn-Si), 17GS (0.17C-Mn), 17G1S, X52: point A means usual KCV level but point B – only a part of *KCV* as the energy for crack propagation.

Fracture mechanics parameters are more sensitive than *KCV*, but it is possible to increase the sensitivity of *KCV* tests by using the crack propagation energy instead of the total energy of fracture [8].

From the other hand, a sensitivity of exploited steels to hydrogen embrittlement increases also, therefore, for the evaluation of its in-service degradation is preferable the hydrogenation conditions, best of all – for the crack growth resistance under action of hydrogenating environment.

A ROLE OF WORKING ENVIRONMENTS IN-BULK MATERIAL DEGRADATION

Investigations of the mechanical properties of the top and bottom areas of the oil and gas pipelines showed that the metal mechanical properties of the bottom areas are worse due to stronger corrosion damage of the inner surface. It means that the water condensed from transported product is not only corrosively aggressive but may also cause material hydrogenation, which is an electrochemical interaction between metal and aqueous environment being a hydrogen source.

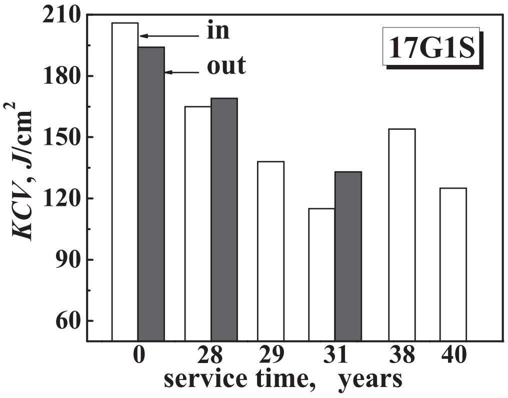

Fig. 3 Impact strength of 17G1S steel after the different time of service: "in" and "out" mean a cut of specimens from pipe wall closer to internal or external surface correspondingly.

Figure 3 shows in *KCV* values for the specimens of in-service main gas pipeline, which were cut close to the external or internal surface. These results prove that the changes of the material properties occur due to the contact with transported product [9].

MECHANISM OF IN-BULK MATERIAL DEGRADATION

Despite of common features, the mechanism of steel degradation is usually distinquished between those at ambient temperature and those at elevated temperature. In the last case the dissolution of martensite with intensive diffusion causes a reduction of pearlite and carbide formation at grain boundary in carbon and low-alloyed steels. These are the main reasons for simultaneous drop of the hardness and strength one hand, and the brittle fracture toughness on the other hand.

According to the widespread opinion, the principal cause of degradation of the main pipelines steels is the deformation aging, which occurs when free carbon migrates to dislocations, settles there and decreases its moveability. The role of free carbon consists also in its moving by diffusion from grain bodies to grain boundaries. Since this process is very slow at ambient temperature it is considered [10] that during decades of pipeline operation carbon can make only 1 μm in direction to grain boundaries, but this is sufficient to create there nano-sized carbides (Fig. 4). It should be noted that hydrogen can intensify carbon migration by accelerating diffusion [11, 12]. Thus hydrogen not only facilitates crack initiation and propagation but also changes material microstructure.

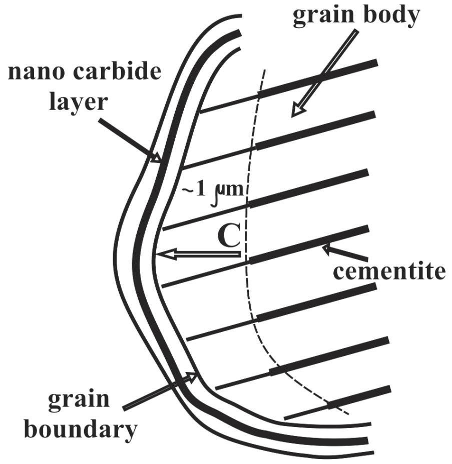

Fig. 4 The model representing the mechanism of in-service degradation of main pipeline steels

The opinion that the material microdamage is the main cause of the degradation of pipelines is consistent with the results of the investigations of hydrogen behaviour in metal obtained by assessing the hydrogen permeability and temperature dependent hydrogen extraction from the steels in different states [1, 3, 13]. These two parameters are very sensitive to defects, which are considered as hydrogen traps and serve as the base of the metal defectiveness analysis. The physical (lattice) D and effective D^* (with regard to trapping) diffusion hydrogen coefficients can be determined and the ratio $D/D^* = 1 + N(k/p)$ can be calculated. Here N is the density of traps, k and p are the kinetic constants of trapping and release of hydrogen from traps, and $N(k/p)$ is the efficiency of hydrogen trapping. Concerning a determination of hydrogen amount in the metal by vacuum extraction with stepwise temperature increase it is posible to distinquish a relatively low temperature, "low-energy" hydrogen, i.e., hydrogen located in low-energy traps (dislocations), and "high-energy" hydrogen located in "deeper" traps (pores, nano-, or microcracks), which leaves such defects at higher temperatures. As it was shown, long-term service of steels causes a decrease of effective diffusion hydrogen coefficient and shifts a temperature, at which the most part of hydrogen lefts metal, in direction to "high-energy" hydrogen.

In-service decrease of grain boudary strength is in agreement with the study of internal friction of the gas pipeline steels X52 in as-received state and after 30 years of service [3]: the observed rise of peaks in the range at 600 – 1050 K indicates about a hampering of relaxation processes on grain (between phases) boundaries due formation there defects.

MATERIAL DEGRADATION AT PIPE WELD JOINTS

The material degradation rate in welds is different in different zones. Therefore it is important to find out which zone is the most sensitive to in-service changes. For example, while it is generally acknowledged that the heat effective zone has particularly low brittle fracture toughness and hydrogen embrittlement resistance, it was find out that the steam pipeline weld material is more sensitive to in-service degradation than the basic material [14]. It means that the weld metal and not the heat affective zone can limit the lifetime of pipelines.

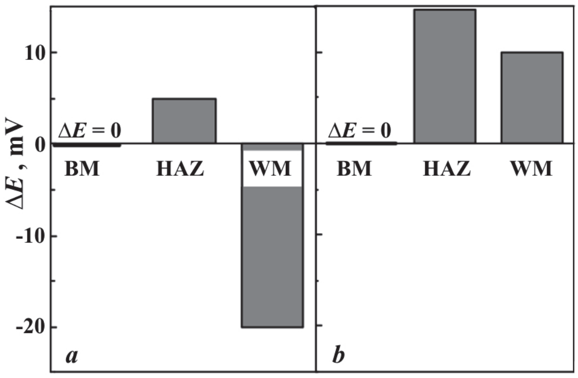

Fig. 5 Electrode potential shift for different zones of 17G1S weld joints of pipes in as-received state (a) and after 30 years of service (b).

It is generally acknowledged that the corrosion process different weld zones depends not only on the material properties in this zone but also on the properties of the neighbor zones due to the effect of galvanic couples. Then in-service change of the electrochemical parameters, i.e. The electrode potential, at different rates for different zones can cause a change of polarity of weld zone (fig. 5). Not only the anodic part in a galvanic couple is dangerous because of additional metal dissolution in this zone but also the cathodic part, where the material hydrogenation can occur. Since after the long term operation the material becomes sensitive to hydrogen embrittlement, this effect can be more important than the increased anodic dissolution.

APPLICATION OF ELECTROCHEMISTRY APPROACHES FOR THE PREDICTION OF MECHANICAL PROPERTIES DEGRADATION

Since a long-term operation alters not only the mechanical properties but also the electrochemical parameters, it was proposed to include this effect for the prediction of in-service degradation of the material state [5, 15, 16]. The electrochemical properties can be measured in field conditions in a non-destructive way. Therefore this approach can be considered as non-destructive testing. Figure 6 demonstrates a good agreement between the mechanical (impact strength) and the electrochemical (polarisation resistance) parameters, both having high sensitivity to the material degradation.

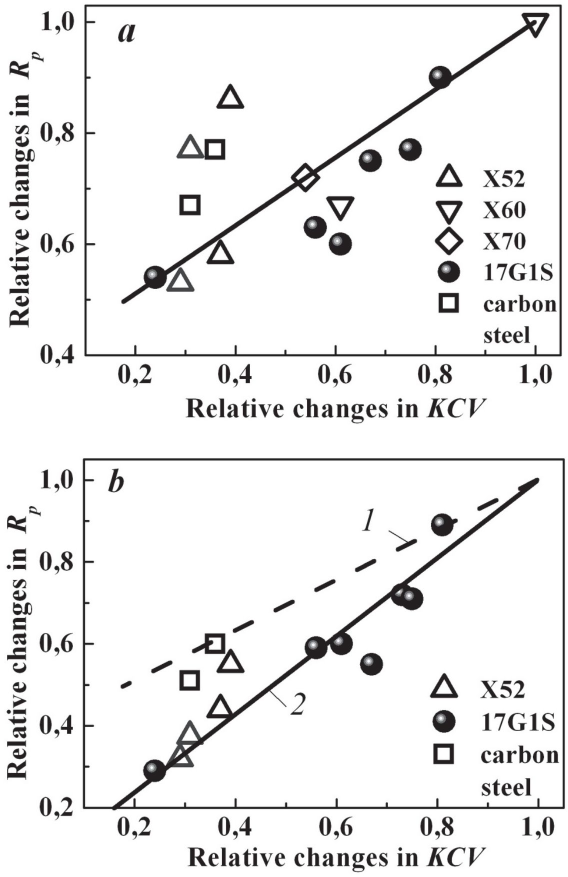

Fig. 6 Correlation between a change of impact strength *KCV* and polarization resistance R_p exploited steels of the main gas pipelines: 17G1S, X52 and low carbon steel in the model environment of gas condensate (a; b, curve 1), X60 and X70 in NS-4 solution (a) and 17G1S and X52 in the proposed solution of pH2 (b, curve 2).

It should be noted that the operation in corrosion environments does not necessarily mean that it can be used as an electrolyte for the prediction of mechanical properties degradation. The service environment is interesting from the point of its role in degradation process, but it may be not the best for the mentioned goal. Therefore a model environment was developed that minimizes formation of protective films on the material surface and increases this way the sensitivity of electrochemical parameters to changes of material state (Fig. 6b).

IN-LABORATORY MODELLING OF DEGRADATION

Normally in the structure design the decision on materials, treatments and welding procedures is based on comparison of material properties in as-received state. However the stability of the physical and mechanical properties during long-term service is very important. It is not sure that the best materials will stay the best after decades of service. Hence the development of in-laboratory methods for accelerated material degradation is a relevant issue.

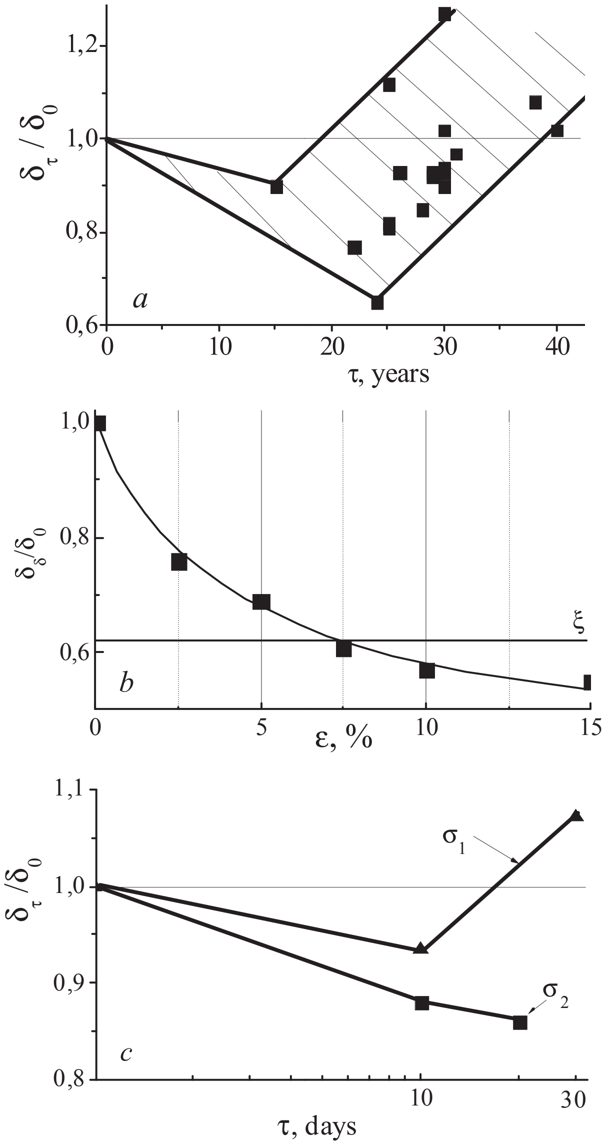

Fig. 7 Test data on elongation during service of main gas pipeline steels (a), after in-laboratory modelling according to GOST 7268-82 Standard (b) and the proposed method at static loading of 300 MPa and 400 MPa during 30 days (c) for 17G1S steel.

The known method consists in the prestraining of specimens up to 10% with the subsequent heating to 250 °C and holding 1 hour during this temperature (USSR Standard GOST 7268-82). This detects the possible process of deformation aging, even during hot covering of pipeline by isolative coating. However the fact that the microdamage of long-term operating steels is the main cause of their in-service degradation should be taken into account. The proposed method consists in: preliminary hydrogenation of specimen by electrolytic charging; electrolytic coating of specimens with copper for hydrogen desorption prevention; holding of specimen up to 30 days under static loads that correspond to the service conditions; holding of specimen at 250 °C for hydrogen desorption and deformation aging.

Figure 7 shows the effectiveness of the proposed method on the example of evaluation of material state, using the elongation δ as plasticity parameter. As it was mentioned above, the elongation decrease does not occur during the whole test period (like the reduction of cross-section area does) because of the in-bulk material dissipated damaging (Fig. 7a). The conventional method provides a monotonic decrease of δ (Fig. 7b), while the proposed method give a non-monotonic decrease (Fig. 7c), which agrees with the test data on steels after different times of operation (Fig. 7a). Since such special dependence of elongation on the operation time is caused by dissipated damaging, it means that with the proposed method, which uses hydrogenation of material, the material degradation in service conditions is well reproduced.

References

[1] H.M. Nykyforchyn, K.-J. Kurzydlowski, E. Lunarska, in: Prediction, Industrial Developments and Evaluations, vol. 2 of *Environment-induced cracking of materials*, Ed. by S.A. Shipilov, R.H. Jones,, J.-M. Olive and R.B. Rebak, Elsevier, (2008), p. 349.

[2] H.M. Nykyforchyn, O.Z. Student, H.V. Krechkovs'ka, A.D. Markov: Mat. Sci., N 2 (2010), p. 177.

[3] H. Nykyforchyn, E. Lunarska, O. Tsyrulnyk et al.: Mat. and Corr., N 9 (2009), p. 716.

[4] H. Nykyforchyn, E. Lunarska, O.T Tsyrulnyk et al.: Eng. Failure Analysis, N 4 (2010), p. 624.

[5] Kryzhanivs'kyi E.I. and Nykyforchyn H.M.: Mat. Sci., N 2 (2011), p. 127.

[6] V.V. Panasyuk, H.M. Nykyforchyn: Proc. of the 19th European Conference on Fracture «Fracture Mechanics for Durability, Reliability and Safety», Kazan, Russia, 26–31 August, 2012. – Paper 77 (CD).

[7] H.M. Nykyforchyn, E. Lunarska, P. Zonta: Proc. of the NATO advanced research workshop on corrosion protection of pipelines transporting hydrocarbons, Dordrecht, Springer (2011), p. 59.

[8] G. Gabetta, H. M. Nykyforchyn, E. Lunarska et al.: Mat. Sci., N 1 (2008), p. 104.

[9] O.T. Tsyrulnyk, Z.V. Slobodyan, O.I. Zvirko et al.: Ibid, N 5 (2008), p. 619.

[10] Yu. S. Nechaev: Uspekhi Fizicheskikh Nauk, N 7. (2008), p. 681.

[11] V.A. Goltsov: Int. J. of Hydrogen Energy, N 2/3 (1997), p. 119.

[12] V. M. Sidorenko, V. V. Fedorov, L. V. Barabash and V. I. Pokhmurskii: Mat. Sci., N 6 (1978), p. 607.

[13] E. Lunarska: Proc. of Int. Conf. Environmental Degradation of Engineering Materials, 1999, Gdańsk, Poland, p. 32.

[14] Zvirko O., Tsyrul'nyk O., Voloshyn V.: Proc. of the 19th European Conference on Fracture «Fracture Mechanics for Durability, Reliability and Safety», Kazan, Russia, 26–31 August, 2012, Paper 142 (CD).

[15] Nykyforchyn H.M., Tsyrulnyk O.T.: Ultrasound, Vol. 64 (2009), p. 46.

[16] H. M. Nykyforchyn, O. T. Tsyrul'nyk: Strength of Materials, Issue 6 (2009), P. 651.

.