ELECTROCHEMICAL HYDROGEN ABSORPTION OF API X52 STEEL AND ITS EFFECT ON LOCAL FRACTURE EMANATING FROM NOTCHES

Originalni naučni rad / Original scientific paper
UDK / UDC: 621.643.027:669.15  620.193.14:669.15
Rad priljen / Paper received: 20.01.2009.

Originalni naučni rad / Original scientific paper
UDK / UDC: 621.643.027:669.15  620.193.14:669.15
Rad priljen / Paper received: 20.01.2009.

Keywords
• hydrogen charging
• hydrogen absorption
• hydrogen concentration
• cathodic polarisation
• current density
• acoustic emission
• static load
• work at local fracture

Abstract

The study of hydrogen-charging process of pipeline steels API X52 grade was performed and local strength of notched samples in presence of hydrogen was determined. The obtained results have shown that this steel is sensitive to hydrogenation in deoxygenated NS4 solution of near-neutral pH value. Applied stress, equal to hoop stress in pipe wall under operating internal pressure 70 bar, significantly accelerates hydrogen charging of steel and hydrogen concentration in loaded steel can be even five times higher than in unloaded steel. It was found that critical hydrogen concentration exists that causes significant reduction of steel local fracture resistance. This value might be applied as an important engineering parameter for reliability assessment of pipelines in exploitation. For local strength assessment of notched samples in presence of hydrogen the diagram “work at local fracture – hydrogen concentration” is convenient and can be accepted as basic curve for considered system “material – environment”.

INTRODUCTION

Nowadays, pipelines for gas and oil transportation are very significant components of national as well as global economic infrastructures. Huge plans for installation of new transcontinental pipelines require increased attention regarding their reliable and safe exploitation. In this frame, the hydrogen degradation of pipeline steels is an important problem for structural integrity for the following reasons.

Specific long-term exploitation of pipelines promotes the steel hydrogenating process. First of all, pipeline steels encounter hydrogen during transport of sour crude oil and other petroleum products, /1/. Moreover, external environmental conditions cause free corroding processes, where hydrogen can be assessed on metal surface as result of cathodic counterpart of the anodic dissolution reaction. This fact was proved in several studies, /2–4/. Under the in-

Julien Capelle¹, Igor Dmytrakh², Guy Pluvinage¹

ELEKTROHEMIJSKA APSORPCIJA VODONIKA U ČELIKU API X52 I NJEN UTICAJ NA LOKALNI LOM IZ ZAREZA

The study of hydrogen-charging process of pipeline steels API X52 grade was performed and local strength of notched samples in presence of hydrogen was determined. The obtained results have shown that this steel is sensitive to hydrogenation in deoxygenated NS4 solution of near-neutral pH value. Applied stress, equal to hoop stress in pipe wall under operating internal pressure 70 bar, significantly accelerates hydrogen charging of steel and hydrogen concentration in loaded steel can be even five times higher than in unloaded steel. It was found that critical hydrogen concentration exists that causes significant reduction of steel local fracture resistance. This value might be applied as an important engineering parameter for reliability assessment of pipelines in exploitation. For local strength assessment of notched samples in presence of hydrogen the diagram “work at local fracture – hydrogen concentration” is convenient and can be accepted as basic curve for considered system “material – environment”.

INTRODUCTION

Nowadays, pipelines for gas and oil transportation are very significant components of national as well as global economic infrastructures. Huge plans for installation of new transcontinental pipelines require increased attention regarding their reliable and safe exploitation. In this frame, the hydrogen degradation of pipeline steels is an important problem for structural integrity for the following reasons.

Specific long-term exploitation of pipelines promotes the steel hydrogenating process. First of all, pipeline steels encounter hydrogen during transport of sour crude oil and other petroleum products, /1/. Moreover, external environmental conditions cause free corroding processes, where hydrogen can be assessed on metal surface as result of cathodic counterpart of the anodic dissolution reaction. This fact was proved in several studies, /2–4/. Under the in-
service condition when a cathodic protection system is applied, hydrogen charging of pipeline steels is also possible /4, 5/. As a result there is the problem of structural integrity of aging buried pipelines having cathodic protection, /5/.

The second reason that attracts the attention to the problem of hydrogen degradation of pipeline steels is the fact that hydrogen can play a decisive role in a future energy system, when fossil fuels have become scarce and thus expensive and/or unsuitable from ecological reasons. The number of aspects related to the technical feasibility and economics of developing a hydrogen energy infrastructure are presented and discussed in literature during last decades /6, 7/. The possible use of existing pipeline networks for mixtures of natural gas and hydrogen offers a unique and cost-effective opportunity to initiate the progressive introduction of hydrogen as a part of the development of a full hydrogen energy system, /6, 8/.

In the present study, the assessment of local strength of notched samples of pipeline steel API X52 has been done in conditions of cathodic hydrogen charging. The relationship between hydrogen concentration and critical (fracture) loading has been found. The existence of critical hydrogen concentration which causes the significant reduction of local fracture resistance of material, has been also proved.

EXPERIMENTAL PROCEDURE

The objects of the study were specimens of API X52 steel, machined from real pipes (diameter D = 610 mm, wall thickness t = 11 mm). Specimens were notched to model the longitudinal external defect exposed to working internal pressure (Fig. 1). Steel chemical composition is given in Table 1, and mechanical properties in air, in Table 2.

Table 1. Chemical composition of API X52 steel (wt. %).

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>0.08</td>
<td>1.06</td>
<td>0.26</td>
<td>0.019</td>
<td>0.003</td>
<td>0.039</td>
</tr>
<tr>
<td>Cu</td>
<td>0.041</td>
<td>0.018</td>
<td>0.02</td>
<td>0.019</td>
<td>0.054</td>
<td>0.003</td>
</tr>
</tbody>
</table>

For the fracture toughness test, the special “Roman tile” specimens, /9/, were used (Fig. 1). Specimens were notched for modelling longitudinal external defects under operating internal pressure (Fig. 2).

Table 2. Mechanical properties of API X52 steel in air.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate tensile strength (UTS)</td>
<td>528 MPa</td>
</tr>
<tr>
<td>Yield stress (YS)</td>
<td>410 MPa</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>30.2</td>
</tr>
</tbody>
</table>

The study was conducted in a special soil solution NS4 with pH = 6.7, /10/. Chemical composition of this environment is given in Table 3. In these conditions, i.e. in deoxygenated, near-neutral pH solution, the hydrogen atoms are generated on the steel surface by electrochemical reduction of water molecules, /2, 3/:

\[ \text{H}_2\text{O} + e^- \rightarrow \text{H}_\text{ads} + \text{OH}^- \]  (1)

The adsorbed hydrogen atoms can subsequently combine into H₂ molecules by the chemical reaction:

\[ 2\text{H}_\text{ads} \rightarrow \text{H}_2 \]  (2)

or the electrochemical reaction:

\[ \text{H}_\text{ads} + \text{H}_2\text{O} + e^- \rightarrow \text{H}_2 + \text{OH}^- \]  (3)

or can be absorbed by the steel:

\[ \text{H}_\text{ads} \rightarrow \text{H}_\text{abs} \]  (4)

Here should be noted that, /2, 3/, the absorbed hydrogen atom concentration under the cathodic polarisation depends on the hydrogen atom recombination mechanisms. When the chemical reaction Eq. (2) dominates the hydrogen atom recombination, the applied cathodic polarisation enhances the generation of hydrogen atoms and thus the amount of hydrogen atoms penetrating into the steel. The absorbed hydrogen atom concentration will increase continuously with cathodic polarisation potential. In the case of electrochemical reaction Eq. (3), dominating the hydrogen atom recombination, the cathodic polarisation promotes the generation of hydrogen atoms through reaction Eq. (1), and simultaneously, enhances the hydrogen atom recombination through reaction Eq. (3). Thus, the role of cathodic polarisation is to generate hydrogen atoms and also to recombine hydrogen atoms.

However, a prevailing number of reported studies, /11-14/, was conducted using cathodic charging of hydrogen under high density of polarisation current. Such charging is not truly representative of the hydrogen entry conditions in...
real operating pipelines, with the situation of a freely corroding system, /15/. This fact is pointed out in Ref. /4/.

Accounting the fact that a steady state condition of hydrogen charging cannot be imposed nor obtained in a freely corroding situation, in the presented study the following procedure is made. Specimens were hydrogen charged at constant polarisation potential $E_{\text{cath}} = -1000$ mV (SCE), which is slightly more negative for tested steel than free corrosion potential $E_{\text{corr}} = -800$ mV (SCE). In this experiment the Potentiostat VMP, /16/, was used.

The specimens were immersed into the cell with special NS4 solution and exposed under constant potential of polarisation $E_{\text{cath}} = \text{const}$. The surface of auxiliary electrode was parallel to notch plane with the distance $h = 20$ mm. The disposition of working (specimen) and auxiliary electrodes is presented in Fig. 3.

![Figure 3. Disposition of electrodes during testing.](image_url)

Specimens were loaded during the hydrogen-charging process. The level of load was defined as gross hoop stress $\sigma_{\text{gross}}$ in pipe wall, which corresponds to the operating internal pipe pressure $P_{\text{op}} = 70$ bar.

The hydrogen-charging process was controlled by registration of the cathodic polarisation current $I_{\text{cath}}(\tau)$. The total quantity of evaluated hydrogen on the metal surface during exposition time $\tau_{\text{exp}}$ can be assessed as:

$$Q_{\text{H}}^{\text{exp}} = \int_{0}^{\tau_{\text{exp}}} I_{\text{cath}}(\tau) d\tau \quad \text{under} \quad E_{\text{cath}} = \text{const}. \quad (5)$$

Hydrogen concentration in metal has been determined on the base of hydrogen discharging process under anodic polarisation using the hydrogen electrochemical oxidation method, proposed in Ref. /17/. Here the standard three-electrode electrochemical cell had been used.

Hydrogen discharging of specimens was carried out in 0.2M NaOH (pH = 12.4) solution under anodic polarisation $E_{\text{anodic}} = +168$ mV (SCE) during defined time $\tau_{\text{dis}}$ (Fig. 4). The total quantity of hydrogen absorbed by metal can be defined as:

$$Q_{\text{H}}^{\text{abs}} = \int_{0}^{\tau_{\text{dis}}} I_{\text{H}}(\tau) - I_{\text{ref}}(\tau) d\tau \quad \text{under} \quad E_{\text{anodic}} = \text{const}. \quad (6)$$

where the anodic polarisation current for hydrogen charged specimen is $I_{\text{H}}(\tau)$ and for specimen without hydrogen (reference curve) is $I_{\text{ref}}(\tau)$. Hydrogen concentration is calculated according to the formula:

$$C_{\text{H}} = \frac{Q_{\text{H}}^{\text{abs}}}{zFv}. \quad (7)$$

Here $z$ is the number of electrons taken in reaction; $F$ is the Faraday constant; $v$ is the effective volume of specimen. Corresponding values in the considered case are as follows: $C_{\text{H}}$ [mol/cm$^3$]; $Q_{\text{H}}^{\text{abs}}$ [A·s]; $z = 1$; $F = 9.65 \times 10^4$ C/mol; $v = 0.256$ cm$^3$.

After assigned exposition under hydrogenating conditions, all specimens were tested to fracture under increasing 3-point bend static loading on testing machine INSTRON at the constant displacement rate $d\Delta/d\tau = 0.02$ mm/s.

The load-displacement diagram and acoustic emission (AE) signal are simultaneously registered by PC during the tests. The fracture initiation is defined by acoustic emission, /18/. The testing scheme is given in Fig. 5.

![Figure 4. Hydrogen discharging process under anodic polarisation.](image_url)

![Figure 5. Schematic view of testing equipment for fracture toughness determining of hydrogen charged specimens: 1—"Roman tile" specimen; 2—loading device of testing machine; 3—corrosion cell with NS4 solution; 4—pH electrode; 5—reference calomel electrode; 6—auxiliary electrode; 7—acoustic emission sensors.](image_url)

RESULTS AND DISCUSSION

Process of hydrogen charging of pipeline steels in given conditions of cathodic polarisation is characterised by the following parameters: hydrogen concentration in metal $C_{\text{H}}$. 
total quantity of evaluated $Q_{ev}$ and absorbed $Q_{abs}$ hydrogen; averaged cathodic current density $i_e$ and efficiency coefficient of hydrogen permeation in metal $k = Q_{abs}/Q_{ev}$.

Comparative evaluation of hydrogen generation process on metal surface and hydrogen permeation in metal for unloaded and stressed specimens have shown intensifying of both processes by applied gross stress $\sigma_{gross}$, corresponding to internal pressure in pipe $p_{exp} = 70$ bar. Although, it can be concluded that the efficiency of hydrogen absorption in metal is quite low and depends on time of exposition. For $r \geq 20$ hours there is the tendency of monotonic decreasing of parameter $k = Q_{abs}/Q_{ev}$, to the level $k = 0.0013 \div 0.0031$ (Fig. 6a). Generally, applied stress increases the hydrogen concentration in metal (Fig. 6b). Hydrogen concentration for $r \geq 100$ hours in stressed steel can be five times higher than in unloaded steel.

Based on experimental results, the increase of hydrogen concentration in metal versus exposition time in the hydrogen-generating conditions can be described by power relation:

$$C_H = A \cdot 10^{-6} \cdot r^m \ [\text{mol/cm}^3]$$  \quad (8)

where $A$ and $m$ are constants (Table 4).

Table 4. Values of constants in Eq. (8).

<table>
<thead>
<tr>
<th>Test conditions</th>
<th>$A$</th>
<th>$m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unloaded metal</td>
<td>0.253</td>
<td>0.24</td>
</tr>
<tr>
<td>Stressed metal</td>
<td>0.300</td>
<td>0.57</td>
</tr>
</tbody>
</table>

The results of fracture toughness experimental study of notched specimens in the presence of hydrogen are given as dependencies of total work of local fracture $W_f^{(total)}$ versus exposition time $r$ of specimens under hydrogenating conditions. The scheme of determination parameters $W_f^{(total)}$ and $W_f^{(plastic)}$ is presented in Fig. 7. Dependencies of these parameters on the hydrogen concentration $c_H$ in metal were also obtained by analytical relation, Eq. (8). The obtained values are given in diagrams (Fig. 8) and in Table 5.

The main observation to be made from these results is existence of some critical exposition time and, as a consequence, critical hydrogen concentration $C_{H(critical)}$, when the substantial decrease of fracture toughness value takes place. Therefore, a concentration of hydrogen in metal defines its local fracture resistance. From this reason the diagram work of local fracture vs. hydrogen concentration can be considered as an invariant curve for a given system “material-environment”. For steel X52 the value of critical hydrogen concentration is $C_H \geq 4.3 \cdot 10^{-6}$ mol/cm$^2$ (Fig. 8a). This value may be considered as an important engineering parameter for reliability assessment of exploited pipelines.

It is to notice that the definition “critical concentration” is often used in studies of problem of hydrogen in metals and alloys /7, 19-21/, although in some references this term has different physical meaning. For example, according to Ref. /19/, hydrogen treatment below the critical content was found to cause the substantial rearrangement of dislocations.
and grain boundaries decohesion, and in overcritical condition, the formation of micro crevices at the grain and phase boundaries. Some authors applied this definition for the development of local fracture criteria, /7, 20/.

At the end, it may be noted that obtained results can be considered as the basis for further investigation with the aim of fracture risk assessment of defected pipelines. It may be done according to modified SINTAP procedure for case of notch, proposed in Ref. /25/, and where a notch-based failure assessment diagrams (NFAD) are developed.

CONCLUSIONS

The study of the hydrogen-charging process of pipeline steels grade API X52 is conducted and its local strength at notches in the presence of hydrogen is determined. The obtained results allowed the following conclusions.

1. The given steel exhibited sensitivity to hydrogenating in NS4 solution, deoxygenated, near-neutral pH, under “soft” cathodic polarisation at $E_{cath} = -1000$ mV (SCE). The efficiency of hydrogen permeation in metal is quite low and depends on time of exposition. It can be stated that for the time $\tau \geq 20$ hours there is a tendency of monotonic decreasing of parameter $k = Q_{abs}/Q_{ev}$, up to the values of $0.0013 \div 0.0031$.

2. Applied stress, equal to gross hoop stress in pipe wall under operating internal pressure 70 bar, significantly accelerates hydrogen charging of steel. There is clear difference of hydrogen concentration in unloaded and stressed metal: it can be five times higher in the stressed steel than in unloaded steel for $\tau \geq 100$ hours.

3. For steel API X52, critical hydrogen concentration exists at the level $C_H \geq 4.3 \cdot 10^{-6}$ mol/cm$^3$, which causes significant reduction of local fracture resistance of the material. This value might be considered as an important engineering parameter for reliability assessment of exploited pipelines.

4. For the assessment of local strength of notched specimen in the presence of hydrogen, the diagram work for local fracture vs. hydrogen concentration is an effective tool and it can be considered as an invariant curve for considered “material–environment” system.
ACKNOWLEDGEMENTS

The presented study is partly performed within the frame of NATURALHY project. Igor Dmytrakh would like to thank Ecole Nationale d’Ingénieurs de Metz (ENIM) and Universite Paul Verlaine Metz for the opportunity to conduct this research.

REFERENCES