

Assessment of steel sensitivity to hydrogen induced cracking

J. Dziubiński, P. Adamiec

Silesian University of Technology, Katowice, Poland

ABSTRACT: *Factors influencing hydrogen induced cracking of transmission pipeline steels are described in the paper. Ratios of hydrogen induced cracking are presented, determined on the basis of metallographic examination, as well as the new hydrogen induced cracking ratio determined on the basis of a static tensile test. A model allowing for an assessment of specimens behaviour with hydrogen induced cracks has been proposed. This model allows to determine the relations between the HIC ratios proposed by NACE TMO 284-96 Standard (metallographic examinations) and the new HIC ratio proposed by authors which expresses the decrease of the plastic properties (contraction) of hydrogenated specimens in relation to non-hydrogenated specimens (strength tests). The presented model has been verified basing on the results of HIC tests of X52, X60, X65, X70 steels.*

INTRODUCTION

The service of welded transmission pipelines for the transport of gas containing moist hydrogen sulfide H_2S may lead to their destruction as a result of the occurrence of hydrogen induced cracks. Hydrogen Induced Cracking (HIC) of welded constructions had been known before, as early as in the 1970s when hydrogen embrittlement in a form susceptibility to cracking was used for the assessment of weldability of, first and foremost, low-alloyed steels.

The currently carried out investigations [1-4] show that HIC may occur also in the native material in a form of hydrogen induced cracks, the mechanism of which is presented in Figure 1.

The source of hydrogen can be moist hydrogen sulfide which as a result of chemisorption and electrochemical reactions diffuses as atomic hydrogen to the pipelines walls, where in the area of material discontinuities and non-metallic inclusions a recombination of hydrogen occurs, combined with an increase of stresses which, when exceeding the cohesion stresses values, lead to HIC.

The following factors can be decisive for HIC of the steel used for transmission pipelines:

- H₂S content in the medium as well as internal pressure and external stresses,
- steel structure after plastic working, where as unfavourable regarded are structures containing bainitic and martensitic regions which occur after thermal and plastic working of steel [2],
- presence of elongated non-metallic inclusions of MnS type, whose contact is conducive to the creation of hydrogen concentration areas of high pressure.

A HIC analysis of X52, X60, X65 and X70 steels has been made, basing on the crack ratios described in NACE standard [5] and on the hydrogen embrittlement ratio proposed by the authors. An attempt to combine these two values has been made.

The American standard NACE TM0284-96 [5] gives the method of HIC evaluation by determining the cracks ratios on metallographic specimens previously subjected to hydrogenation. These ratios are: CSR (Crack Sensitivity Ratio), CLR (Crack Length Ratio) and CTR (Crack Thickness Ratio).

A relative crack length ratio (Figure 2, Eq. 1) is the ratio of the total sum of single cracks a_i to the specimen section width W :

$$\text{CLR (Crack Length Ratio)} = \frac{\sum a_i}{W} \cdot 100\% \quad (1)$$

A relative crack sensitivity ratio (Eq. 2) is the ratio of the total sum of every stepped cracking area $a_i \cdot b_i$ to the section area of the specimen under observation:

$$\text{CSR (Crack Sensitivity Ratio)} = \frac{\sum (a_i \cdot b_i)}{W \cdot T} \cdot 100\% \quad (2)$$

where a_i , b_i are the length and thickness of the stepped cracks group, whereas W and T are the width and thickness of the specimen section, respectively.

A relative crack thickness ratio (Eq. 3) is the ratio of the stepped cracks group thickness to the specimen section thickness T :

$$\text{CTR (Crack Thickness Ratio)} = \frac{\sum b_i}{T} \cdot 100\% \quad (3)$$

These ratios are used when designing reliable structures to work in an environment containing acid H₂S. An example can be the requirements of the MG ENGINEERING LURGI design office which for the steels used for the above-mentioned structures (category 4) gives the following criteria: CLR ≤ 15%, CTR ≤ 5% and CSR ≤ 2%.

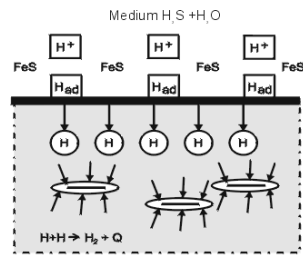


Figure 1: HIC mechanism

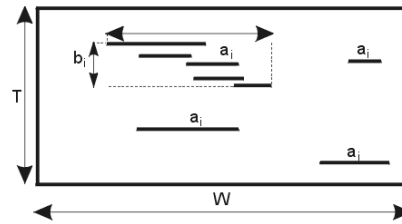


Figure 2: Method of cracks measurement on microsections

Sensitivity to HIC may be also defined by means of the hydrogen embrittlement ratio (Eq. 4) expressed by the following relation:

$$F = \frac{Z - Z_H}{Z} \cdot 100\% \quad (4)$$

where: Z – contraction of non-hydrogenated specimens, Z_H – contraction of hydrogenated specimens.

THE PROBLEM MODEL

The problem model can be a plate with numerous cracks situated on average at a distance „c” from one another (Figure 3a) and visible on the section in a form of cracks of a_i length (Figure 3b).

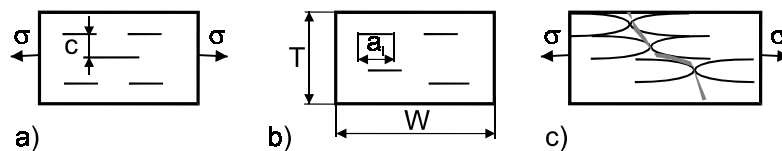


Figure 3: The problem model: a) plate of T thickness with numerous cracks, b) visible cracks on the plate section of W x T dimensions, c) fibrous rupture of plate

In such a model the contraction may occur on the slip lines between cracks, leading to fibrous rupture (Figure 3c). The elongation during contraction undergoes a reduction through internal necks from „T” to „c”, whereas the section measured during the contraction to the internal neck reduces from „T” to „c/T” [6]. In connection with that, when $c \ll T$, the material has a macroscopically „brittle” appearance at the moment when the strength of material is achieved, even when it is in fact microscopically ductile.

Analysing the contraction of a material with cracks (Figure 3a), one can find that the contraction will depend on the number of cracks (LP) visible on the section (Figure 3b) on T thickness. If LP equals 0, the value $c/T = T/T = 1$ and the contraction at tension will reach a certain Z value. If LP is equal e.g. 10, then $c/T = 0,1$ and the macroscopic contraction will amount approximately to $Z_H \cong 0$. By introducing the notion of the contraction reduction coefficient, i.e. the hydrogen embrittlement ratio (Eq. 4), the change of F value can be predicted with the change of the number of cracks (LP). These cracks will divide the specimen into „n” strips. The number of strips is to some extent connected with the hydrogen cracking ratio, CLR. Basing on own investigations presented later in the paper and the examinations presented in paper [7], which concern the decrease of materials contraction Z_H with an increase of non-metallic inclusions content f (the content of inclusions in this case equals CLR, since hydrogen induced cracks occur mainly on non-metallic inclusions) it has been found that an exemplary relation $n = 10$ (CLR) can be proposed, where CLR is the ratio of individual cracks sum to the specimens width (Figure 4).

Analysing the contractions of material with cracks which divide, e.g. a square specimen of $W \times W$ section into „n” strips (Figure 5), assuming that: $W = nD$, $D/d = a$, $A_o = W^2$, $A_k = w^2$ the following relation (Eq. 5) can be formulated:

$$Z_H = \frac{A_o - A_k}{A_k} = \frac{W^2 - w^2}{W^2} = 2\left(\frac{b}{n}\right) - \left(\frac{b}{n}\right)^2 \quad (5)$$

where: $b = 1 - \frac{1}{a}$

Taking into account that $n = 10$ (CLR) the following relation (Eq. 6) can be formulated:

$$F = \frac{Z - \left[2 \left(\frac{b}{10CLR} \right) - \left(\frac{b}{10CLR} \right)^2 \right]}{Z} \quad (6)$$

where: CLR – dimensionless ratio, not expressed in %.

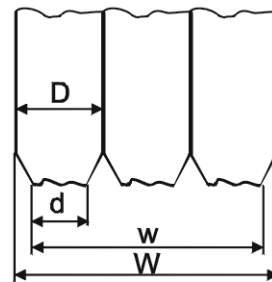
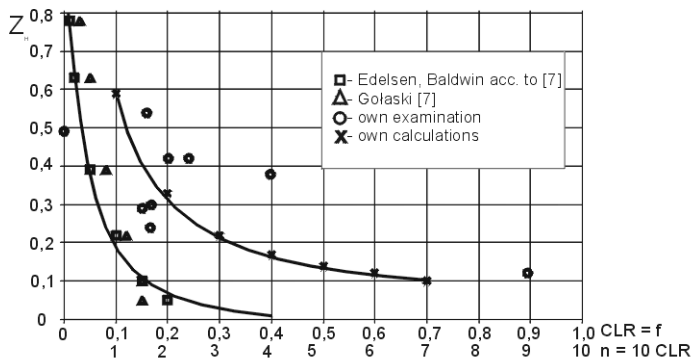


Figure 4: Change of contraction Z_H as a function of CLR, non-metallic inclusions content f and the number of strips n

Figure 5: Model of a specimen with cracks for contraction analysis

EXAMINATION AND CALCULATION RESULTS

Steels destined for pipelines with chemical constitutions and mechanical properties compiled in Table 1 were used in the examination. Specimens from the examined steels were subjected to hydrogenation on a stand presented in Figure 6.

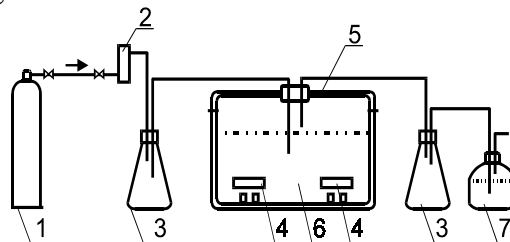


Figure 6: Scheme of the stand for specimens hydrogenation acc. to NACE TM0284–96 standard: 1 – H_2S cylinder, 2 – flowmeter, 3 – protective tanks, 4 – specimens, 5 – specimens hydrogenation reactor, 6 – hydrogenation solution, 7 – H_2S absorber

After the hydrogenation process the specimens contraction Z_H was determined as well as the ratios CTR, CLR and CSR respectively, by means of mechanical and metallographic examination [5]. The examination results are compiled in Table 2 and in Figure 7. The results of calculations according to Eq. 6 are also given in Figure 7. HIC examples in the area of non-metallic inclusions of MnS type and in the area of bainitic and martensitic bands are presented in Figure 8.

TABLE 1: Chemical constitutions and mechanical properties of examined steels

Item	Steel grade thickness mm	Chemical constitution %			R_e MPa	A %	Z %
		C	Mn	S			
1	X52/10	0,17	1,16	0,003	377	25	60
2	X52/12	0,17	1,13	0,003	367	23	30
3	X52/16	0,18	1,14	0,002	373	23	60
4	X52/15	0,19	1,26	0,012	420	41	47
5	X52/8	0,20	1,29	0,012	348	25	68
6	X60/6,3	0,09	1,29	0,002	500	23	49
7	X60/8,7	0,12	1,21	0,009	433	29	50
8	X65/15	0,095	1,61	0,0012	535	31	44
9	X70/20	0,098	1,64	0,0015	486	30	36

TABLE 2: Results of specimens examination before and after hydrogenation

Item	Steel grade thickness mm	$Z\% / Z_H\%$	$F = \frac{Z - Z_H}{Z} \cdot 100\%$	CSR %	CLR %	CTR %
1	X52/10	60/38	37	1,06	30,91	10,35
2	X52/12	60/42	30	0,07	24,12	1,58
3	X52/16	64/54	15	0,09	15,11	2,21
4	X52/15	47/29	38	0,01	15,14	0,40
5	X52/8	68/42	38	-	20,21	-
6	X60/6,3	49/49	0	0	0	0
7	X60/8,7	50/30	40	1,57	16,82	5,25
8	X65/15	44/24	45	0,06	16,61	0,90
9	X70/20	36/12	67	0,52	89,51	2,80

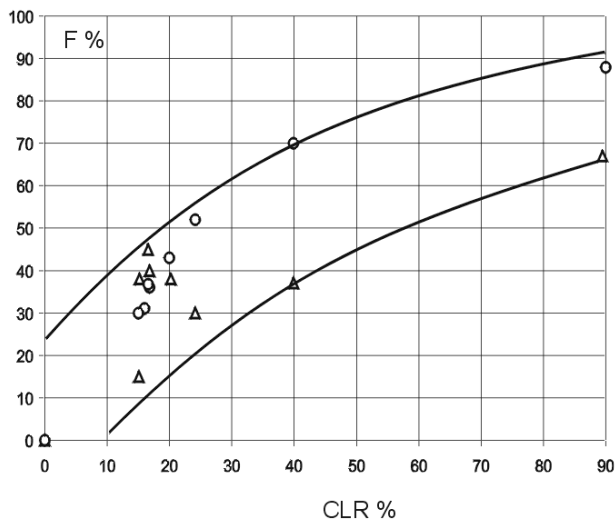


Figure 7: Hydrogen embrittlement ratio F versus CLR
 Δ – experiment, o – calculations

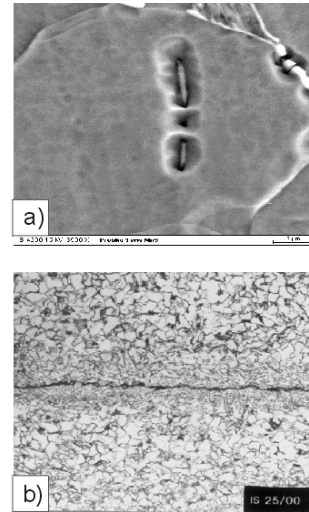


Figure 8: HIC in non-metallic inclusions area (a) and in bainitic and martensitic bands area (b)

ANALYSIS OF RESULTS

A model has been developed to allow for an evaluation of the behaviour of specimens with HIC (Figure 5). This model allows to specify the dependence between the HIC ratios determined by metallographic methods according to standard [5] and the hydrogen embrittlement ratio F (Eq. 4) determined by strength tests. The presented model was verified basing on the results of HIC tests of X52, X60, X65 and X70 steels, for which mechanical properties were determined, among others Z and Z_H and the hydrogen embrittlement ratio, as well as HIC ratios according to standard [5].

In hot rolled steels of X52 and X60 type, the presence of HIC was detected in the area of non-metallic inclusions of MnS type, whereas in X65 and X70 steels the presence of HIC was detected in the areas of martensitic and bainitic bands (M-B), i.e. in the areas with a high degree of plastic strain, which were formed during thermal and mechanical working of these steels (Figure 8). HIC in M-B bands occurred even at a small content of sulfur below 0,002%.

CLR was changing in the examined steels from 0 to 90% and clearly effected the reduction of specimens contraction after hydrogenation Z_H , consequently effecting the hydrogen embrittlement ratio F (Table 2, Figure 7).

The developed model was used to achieve a dependence $F = f(\text{CLR})$ (Eq. 6) of a parabolic nature which was verified experimentally (Figure 7). Such a dependence allows for a transformation of HIC ratios determined by metallographic methods into the results of standard tensile tests (determination of Z).

Moreover, it has been shown in the paper [8] that a safe and simple method of electrolytic hydrogenation can be applied in order to produce HIC instead of complex and restricted by safety regulations hydrogenation performed by means of H_2S (Figure 6).

CONCLUSIONS

1. HIC ratios evaluated on the basis of metallographic examination can be replaced with the hydrogen embrittlement ratio F determined on the basis of tensile tests.
2. Hydrogen induced cracks are located on non-metallic inclusions, in case of normalized hot rolled steels, or in bainitic and martensitic bands in case of steels which have undergone thermal and mechanical working.
3. Electrolytic hydrogenation of specimens brings about hydrogen induced cracks, like in case of specimens hydrogenation by means of H_2S .

REFERENCES

1. Adamiec, P., Dziubiński, J. (2000) *Przegląd Spawalnictwa* **4**, 5.
2. Mazur, A., Dubiel, M. (1995) *Przegląd Spawalnictwa* **12**, 13.
3. Tasak, E. (1992) *Przegląd Spawalnictwa* **7**, 11.
4. Pressouyre, G., M. (1982) In: *Proc. of III Int. Congress on Hydrogen and Materials* pp. 461-466, Paris.
5. NACE Standard TM0284-96. *Assessment of Pipeline and Pressure Vessel Steels for Resistance to Hydrogen Induced Cracking*.
6. Cottrell, A., H. (1964) *The Mechanical Properties of Matter*. John Wiley & Sons Inc., New York.
7. Gołaski, L. (1992) *Elements of Experimental Fracture Mechanics*. Wydawnictwo Politechniki Świętokrzyskiej, Kielce.
8. Dziubiński, J., Adamiec, P. (2000) *Przegląd Spawalnictwa* **6**, 3.