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Hydrogen degradation of high strength weldable steels

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Properties

ABSTRACT

Purpose: Purpose of this paper is presentation of hydrogen degradation issue of high strength steels and especially their welded joints. Establishing of applicable mechanisms of hydrogen-enhanced cracking was the aim of performed research.
Design/methodology/approach: High strength quenched and tempered steels grade S690Q were used. Welded joints were prepared with typical technology used in shipyards. Susceptibility to hydrogen degradation in sea water under cathodic polarization was evaluated with the use of mechanical tests. Various kinds of loads were applied, i.e. monotonically increasing static, constant, and cyclic. Appropriate measures of hydrogen degradation were chosen and analyzed. Mechanisms of hydrogen degradation were detected and established on the basis of scanning electron microscopy (SEM) observation of fracture samples surface.
Findings: Tested high strength steels and their welded joints are susceptible to hydrogen embrittlement when evaluated using a slow strain rate test (SSRT). On contrary, these steels and welded joints have high resistance to hydrogen delayed cracking under a constant load test. Significant reduction of a fatigue life time due to hydrogen absorption has been observed during severe low-cycle fatigue tests.
Research limitations/implications: There is no possibility to perform direct observation of exact hydrogen-assisted cracking mechanisms in massive samples. Valid hydrogen-enhanced cracking model could be only deducted from degradation evidences like plasticity loss and fracture modes.
Practical implications: Tested quenched and tempered S690Q steel grades could be safely utilized for marine welded constructions under cathodic polarization. Hydrogen-assisted cracking should not occur unless a huge overprotection and plastic deformation take place.
Originality/value: Hydrogen-enhanced localized plasticity (HELP) model is the most applicable mechanism of hydrogen degradation for weldable steels with yield strength up to 1000 MPa.
Keywords: Crack resistance; High strength steels; Welded joints; Hydrogen degradation

1. Introduction

High-strength steels have been widely used in construction of large scale welded-structures. The principal advantage of these steels is good combination of strength and toughness. High strength steels are especially suitable for application in pipelines, offshore facilities, and naval vessels and ships.

High strength steels are produced as: quenched and tempered, Thermo Mechanical Control Processed (TMCP), or precipitation hardened with copper. Especially, quenched and tempered steels are thought to be sensitive to hydrogen degradation, which could be a significant limitation of their use [1,2].

Most high strength steels are thought to be susceptible to hydrogen embrittlement when they are stressed and exposed to hydrogen generating environments. The susceptibility of steels to hydrogen degradation generally increases with increasing tensile strength. Steels with tensile strength less than 700 MPa appear to be resistant to hydrogen cracking, and constructions made with such steels have been used in service without serious problems in various environments. Steels having a tensile strength greater than 1000 MPa are susceptible to hydrogen embrittlement, and steels with tensile strength over 1200 MPa are especially susceptible and may fail at stress much below their yield strength. This behavior is termed hydrogen delayed cracking [3-6].

A number of failures due to hydrogen have been reported, e.g. of car engines parts [7,8], ship engines [9,10], and offshore mobile drilling platforms [11,12].

The sources of hydrogen in steel are many: gaseous hydrogen, liberation of atomic hydrogen by the iron-water or iron-H_2S reactions, electrolytic and corrosion processes including a cathodic reaction. Corrosion of marine constructions is prevented by coatings and cathodic protection. The later may be harmful for steels resulting in their hydrogen embrittlement [13].

Hydrogen degrades properties of steels mainly by delayed cracking at stress below the yield strength and by the loss of ductility in a tensile test as reflected by a decreased reduction in area which is generally called hydrogen embrittlement (HE). When local hydrogen concentration is high enough (reaches critical concentration) it may cause hydrogen induced cracking (HIC) or may manifest as advancement of crack propagation (crack has been initiated by mechanical damage or corrosion). Hydrogen effect is greater near room temperature and decreases with increasing strain rate. Hydrogen degradation is more pronounced with increasing hydrogen content or charging rate and with increasing strength of steel [14].

The numerous mechanisms have been proposed to explain LTHA phenomena, which reflect the many ways in which hydrogen was observed to interact with metals [14-16].

2. Materials and experimental procedure

Quenched and tempered plates 12 mm in thickness made of 17HMBVA and 14HNMBCu steel grades – S690Q with minimum yield strength of 690 MPa according to PN-EN 10137-2 [17] was used. Submerged arc welded (SAW) and shielded metal arc welded (SMAW) joints were prepared.

Susceptibility to hydrogen degradation in sea water under cathodic polarization was evaluated with the use of mechanical tests. Various kinds of loads were applied, i.e. monotonically increasing static, constant, and cyclic.

In order to estimate susceptibility to hydrogen embrittlement of tested steel and their welded joints, slow strain rate test (SSRT) according to PN-EN ISO 7539-7 [18] was conducted on round smooth specimens 4 mm in diameter.

Welded joints were placed in the centre of the specimens. Specimens were cut along the transverse direction. Tests were performed at ambient temperature either in dry air or in standard artificial sea-water grade A prepared according to PN-66/C-06502 [19]. The applied strain rate was 10^{-6} s^{-1}. Tests in sea-water were conducted at open circuit potential and under cathodic polarization with constant current densities. The following cathodic currents were applied: 0.1; 1; 10; 20 and 50 mA/cm^2.

Elongation, reduction in area, fracture energy and additionally tensile strength were chosen as measures of hydrogen embrittlement. Then, relative parameters determined as the ratio of the appropriate value measured in air to that measured in artificial sea-water were calculated.

For estimation of resistance to hydrogen delayed cracking of 14HNMBCu steel and the welded joints, the constant load test on round notched specimens 6 mm in diameter was conducted along with PN-EN 2832 [20]. For samples with welded joints, welds were placed in the centre of specimens and a notch was cut in the fusion line. All specimens were cut along the transverse direction. Tests were performed at room temperature in standard artificial sea-water grade A. Tests in sea-water were conducted at open circuit potential and under cathodic polarisation with constant current densities. The following cathodic currents were applied: 0.1; 1; 10 mA/cm^2 giving cathodic hydrogen charging of specimens during a test.

Time to failure of specimen was recorded. When a sample did not fail within 200 hours, the test was ended and result was signed as negative (-) according to PN-EN 2832. When a sample failed premature (before 200 hours), the result was signed as positive (+). Presence or lack of delayed failure of samples was chosen as measures of hydrogen degradation – susceptibility or resistance to delayed hydrogen cracking. Applied loads were calculated as a ratio of actual force (F) to the maximum force (F_m) obtained from a tensile test. Tensile test was performed with slow strain rate 10^{-6} s^{-1} in air using the same notched samples as for a constant load test.

Low-cycle corrosion fatigue tests were performed according to PN-84/H-04334 [21] on cylindrical smooth specimens 4 mm in diameter with 50 mm gauge length. Sinusoidal wave form uniaxial tension loading under strain control (R = 0, positive strain amplitude $\Delta\varepsilon$ = 0.5%, 0.8%, 1%, 2%, and 4%) was carried out at frequency 0.1 s^{-1}. Tests were performed at room temperature either in ambient air or standard artificial sea-water under cathodic polarization. Applied current density of 10 mA/cm^2, giving the highest degradation of plasticity was chosen from previously performed SSRT research.

Mechanisms of hydrogen degradation were detected and established on the basis of scanning electron microscopy (SEM) observation of fracture samples surface.

3. Results and discussion

Examples of obtained results for loss of elongation after SSRT tests presents Fig. 1. Observed decrease of relative values of elongation with the increase of current density exhibits a certain minimum. Further increase of current density does not cause higher degradation due to deposits evolution on samples surface and hindering of hydrogen absorption. The loss of elongation was as high as 40-45% for base metals, 40-55% for SAW, and 55-70 for SMAW joints.

Failure of samples with welded joints occurred always in weld metal, where strength was lower comparing to base metal. The reduction of ductility by hydrogen was accompanied by a change in fracture mode. For samples tested in air crack growth occurred in a ductile mode. Base metal samples tested in air had mixed - quasi-cleavage and micro void coalescence (MVC) fracture.

Under cathodic polarization base metal changed fracture mode, i.e. portion of quasi-cleavage fracture increased, and cleavage fracture also appeared at higher current densities.

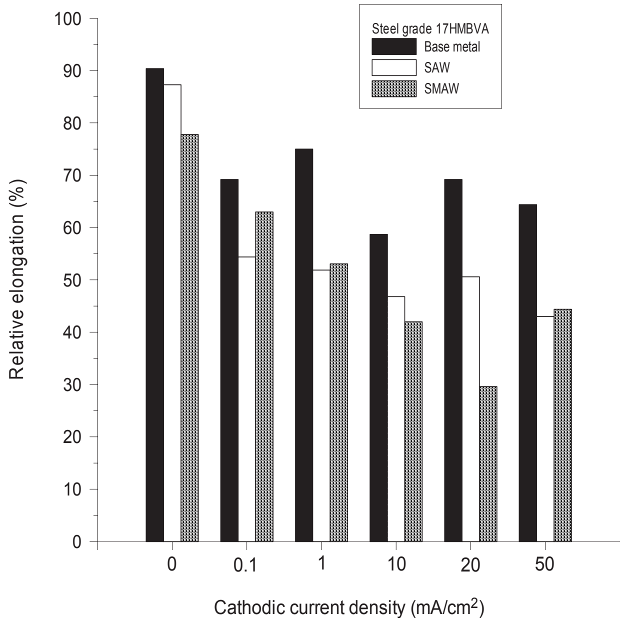

Fig. 1. Relative elongation vs. cathodic current density for 17HMBVA steel and its welded joints

Samples with welded joints tested in air revealed ductile – MVC fracture mode. When cathodic polarization was applied mixed – MVC and quasi-cleavage fracture was observed. At higher cathodic current densities the presence of hydrogen induced microcracks and flakes in weld metal (Fig. 2).
Obtained results of SSRT test and fractographic observations suggest that hydrogen-enhanced localized plasticity (HELP) model is the more applicable mechanism of hydrogen degradation. Hydrogen assisted-cracking occurs at load level as high as flow stress (yield strength) of tested steel and its welded joints.

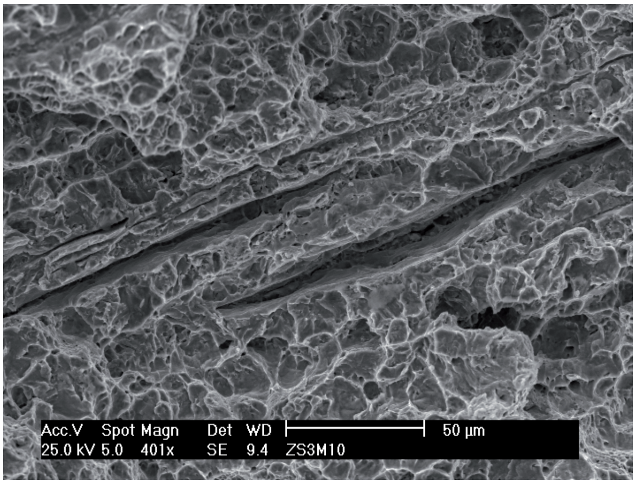

Fig. 2. SEM image of fracture surface of 17HMBVA steel sample with SAW welded joint after SSRT test in seawater, i = 10 mA/cm^2. Fracture localized in weld metal

Ductile and quasi-cleavage fracture modes support suggestion that hydrogen interacts with dislocations and increase their mobility, and at the same time hydrogen is transported by mobile dislocations. Hydrogen ions transported with mobile dislocations locally increasing hydrogen concentration which facilitates cracking.

Some results of the constant load tests are presented in Tables 1-2.

Table 1.
Resistance to delayed hydrogen cracking of 14HNMBCu steel under a constant load test in sea water

Cathodic current density mA/cm^2	Applied relative load F/F$_m$ 0.84	0.88	0.92	0.96
open circuit potential	-	-	-	+
0.1	-	-	+	+
1	-	-	+	+
10	-	+	+	+

"-" means no failure within 200 hours; "+" means premature failure and susceptibility to delayed hydrogen cracking

Table 2.
Resistance to delayed hydrogen cracking of welded joints (SAW) of 14HNMBCu steel under a constant load test in sea water

Cathodic current density mA/cm^2	Applied relative load F/F$_m$ 0.84	0.88	0.92	0.96
open circuit potential	-	-	-	+
0.1	-	-	-	+
1	-	-	+	+
10	-	-	+	+

Steel 14HNMBCu tested in seawater both at open circuit potential and cathodic polarization has high resistance to hydrogen degradation. Additionally, high critical load at the level of 0.96 at open circuit potential shows that tested steel and its welded joints are not susceptible to pitting corrosion in seawater environment.

Submerged arc welded joint (SAW) has higher resistance to hydrogen degradation then base metal. However, shielded metal arc welded (SMAW) joint is more susceptible then base metal. Differences in resistance to hydrogen delayed cracking could be explained by variations of microstructure present in steel and welded joints. The various microstructures resulting in different mechanical properties (strength, hardness) of steel, and its different susceptibility to hydrogen degradation.

Results of fatigue tests of 14HNMBCu steel and its welded joints are presented in Fig. 3. Significant reduction of fatigue life time (30-90%) due to hydrogen absorption was observed for 14HNMBCu steel. Reduction increased with increase of strain amplitude. Welded joints of 14HNMBCu steel had higher resistance to low-cycle fatigue assisted by hydrogen. It should be noted that low-cycle fatigue test is very severe since plastic deformation is reached.

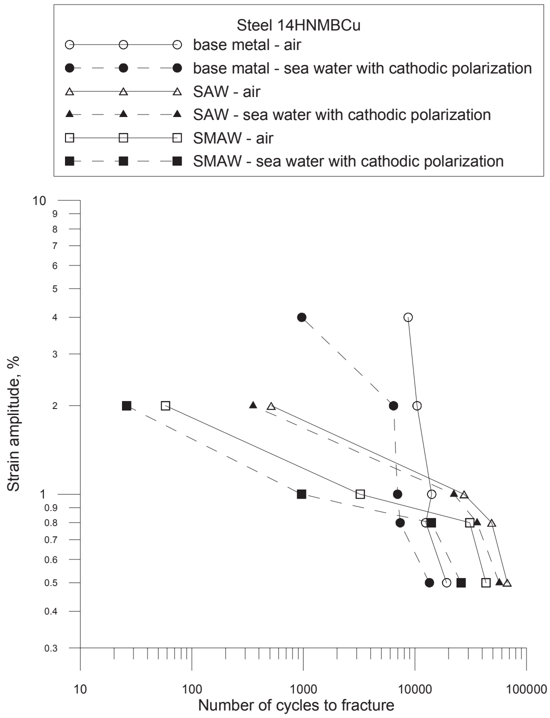

Fig. 3. Number of cycles to fracture versus strain amplitude for 14HNMBCu steel and its welded joints

4. Conclusions

Tested high-strength steel and its welded joints are susceptible to hydrogen embrittlement when evaluated with the use of SSRT. The loss of plasticity is higher for welded joints then for the base metal. On contrary, these steels and welded joints have high resistance to hydrogen delayed cracking under a constant load test. Significant reduction of a fatigue life time due to hydrogen absorption has been observed during severe low-cycle fatigue tests.

Tested quenched and tempered S690Q steel grades could be safely utilized for marine welded constructions under cathodic polarization. Hydrogen-assisted cracking should not occur unless a huge overprotection and plastic deformation take place.

Hydrogen-enhanced localized plasticity (HELP) model is the most applicable mechanism of hydrogen degradation for weldable steels with yield strength up to 1000 MPa.

References

[1] J. Ćwiek, High strength weldable steels, Mechanical Review 9 (1996) 9-15 (in Polish).

[2] J. Ćwiek, Hydrogen assisted cracking of high-strength weldable steels in sea-water, Journal of Materials Processing Technology 164-165 (2005) 1007-1013.

[3] ASM Handbook. Vol. 11 Failure Analysis and Prevention. ASM Int., 1986.

[4] N. Eliaz, A. Shachar, B. Tal, D. Eliezer, Characteristic of hydrogen embrittlement, stress corrosion cracking and tempered martensite embrittlement in high-strength steels, Engineering Failure Analysis 9 (2002) 176-184.

[5] B. Świeczko-Żurek, S. Sobieszczyk, J. Ćwiek, A. Zieliński, Evaluation of susceptibility of high-strength steels to hydrogen delayed cracking, Journal of Achievements in Materials and Manufacturing Engineering 18 (2006) 243-246.

[6] J. Ćwiek, A. Zieliński, Mechanism of hydrogen enhanced-cracking of high-strength steel welded joints, Journal of Achievements in Materials and Manufacturing Engineering 18 (2006) 207-210.

[7] S.P. Lynch, Failures of structures and components by environmentally assisted cracking, Engineering Failure Analysis 2 (1994) 77-90.

[8] S. Sobieszczyk, E. Łunarska, J. Ćwiek, A. Zieliński, K. Nikiforow, Hydrogen charging of plasma nitrided steel in acid solution, Journal of Achievements in Materials and Manufacturing Engineering 17 (2006) 205-208.

[9] A. Zieliński, J. Ćwiek, M. Błaszkiewicz, Effect of plasma nitrided layers on low-alloy steel on its hydrogen degradation, Journal of Achievements in Materials and Manufacturing Engineering 17 (2006) 213-216.

[10] A. Zieliński, E. Łunarska, P. Michalak, W, Serbiński, Strength degradation of 26H2MF and 34HNM steels used in ship engines: hydrogen factor, Materials Science 6 (2004) 822-830.

[11] J.V. Sharp, J. Billingham, M.J. Robinson, The risk of high-strength steels in jack-ups in seawater, Marine Structures 14 (2001) 537-551.

[12] K. Banerjee , U.K. Chatterjee, Hydrogen embrittlement of a HSLA-100 steel in seawater, ISIJ International 1 (1999) 47-55.

[13] R.A. Oriani, J.P. Hirth, M. Smialowski (eds.), Hydrogen Degradation of Ferrous Alloys, Noyes Publ. Park, Ridge, USA, 1985.

[14] P.F. Timmins, Solutions to hydrogen attack in steels, AMS Int., 1997.

[15] H.K. Birnbaum, I. M. Robertson, P. Sofronis, D. Teter, Mechanisms of hydrogen related fracture. A review, Proc. 2nd Int. Conf. Corrosion Deformation Interaction, The Institute of Materials, London (1997) 172-195.

[16] J.P. Hirth, Effects of hydrogen on the properties of iron and steel, Metallurgical Transactions A, 11A (1980) 861-890.

[17] PN-EN 10137-2:2000 Plates and wide flats made of high yield strength structural steels in the quenched and tempered or precipitation hardened conditions - Delivery conditions for quenched and tempered steels.

[18] PN-EN ISO 7539-7:2000 Corrosion of metals and alloys - Stress corrosion testing - Part 7: Slow strain rate testing.

[19] PN-66/C-06502. Substitute seawater.

[20] PN-EN 2832:2001 Aerospace series - Hydrogen embrittlement of steels - Notched specimen test.

[21] PN-84/H-04334 Low-cycle fatigue testing for metals.