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HYDROGEN DELAYED CRACKING OF HIGH-STRENGTH WELDABLE STEELS

ABSTRACT

Hydrogen degradation of high-strength steel and their welded joints was evaluated under constant load mode in sea-water. Tests were carried out using round notched specimens in sea-water at open circuit potential and under cathodic polarisation.

14HNMBCu steel grade with minimum yield strength of 690 MPa, and their submerged arc welded (SAW) and shielded metal arc welded (SMAW) joints were examined.

Presence or lack of delayed failure of samples was chosen as measures of hydrogen degradation. Fracture modes were investigated with the use of a scanning electron microscope (SEM).

Keywords: *hydrogen embrittlement; hydrogen delayed cracking; high-strength low-alloy steel; seawater; cathodic polarisation*

INTRODUCTION

High-strength low-alloy (HSLA) steels have been widely used in construction of large scale welded-structures. The principal advantage of these steels are good combination of strength and toughness, but also their relatively good weldability. Therefore HSLA steels are suitable for application in:

- civil engineering (buildings),
- engineering structures, especially mining and dredging equipment,
- bridges,
- heavy duty trucks, earth moving equipment, and mobile cranes,
- pressure vessels,
- pipelines,
- offshore facilities,
- naval vessels and ships.

High-strength steels are produced as: quenched and tempered, direct quenched and tempered (the kind of TMCP - Thermo Mechanical Controlled Process), or precipitation hardened with copper. Especially, quenched and tempered steels are thought to be sensitive to hydrogen degradation. Significant limitation of use of extra high strength steels could be their hydrogen degradation.

Since a hull of ship or offshore construction is cathodically protected against corrosion, usually by coupling with zinc, cathodic hydrogen is produced on surface and enters material. Several papers have reported hydrogen enhanced cracking of high-strength steels under cathodic charging. A decrease in K_{ISCC} value with more negative potentials has been observed [1].

With respect to hydrogen stress cracking, most susceptible materials show a major effect of stress concentration (i.e. notches) and level of stress intensity, and tend to produce failures in a relatively short time below 1000 hours. Therefore tension, notched, and precracked specimens and fracture methods are widely utilised in the evaluation of hydrogen delayed cracking.

The aim of the paper is to evaluate susceptibility to hydrogen delayed cracking of 14HNMBCu steel and its welded joints.

HYDROGEN DEGRADATION PHENOMENON

Synergic action of stress and environment may result in various types of degradation of metallic materials, including hydrogen-enhanced degradation. Harmful influence of hydrogen at temperatures below 200°C is expressed as low temperature hydrogen attack (LTHA). 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 decreased reduction in area which is generally called hydrogen embrittlement (HE). When local hydrogen concentration is high enough (approaching 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.

With respect to microstructure of ferritic steels, susceptibility to hydrogen degradation increases successively for structures: spheroidised (with fine carbides) → quenched and tempered (Q&T) → normalised and tempered (e.g. ferrite with bainite) → normalised → untempered bainite → untempered martensite.

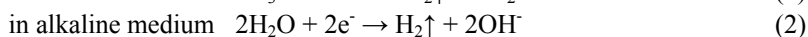
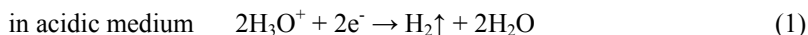
Fine and rounder carbide shapes (Q&T or spheroidised structures) are more resistant than coarser and more angular ones (pearlite). However, coarse spheroidised structure was found to be more susceptible to hydrogen degradation than less tempered structure or fine-grained normalised structure.

Hydrogen cracking may proceed by all microstructural modes, including: ductile fracture, quasicleavage, transgranular cleavage, and brittle intergranular fracture [2,3]

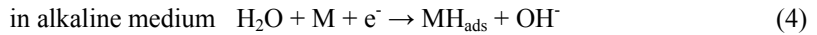
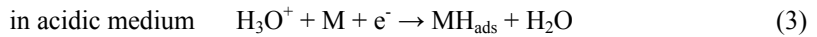
SOURCES OF HYDROGEN IN STEEL

The sources of hydrogen in steel are numerous: gaseous hydrogen, liberation of atomic hydrogen by the iron-water or iron-H₂S reactions, decomposition of water molecules, electrolytic and corrosion processes including cathodic reaction.

During pickling in mineral acids, cathodic electrochemical cleaning, cathodic polarisation protection, and zinc or cadmium plating hydrogen is formed. In all cases it is due to cathodic reduction. The anodic counter reaction in case of pickling is dissolution of metal that takes place at the same location as evolution of hydrogen. In case of electrolytic cleaning, cathodic polarisation or electrolytic plating, the counter reaction is formation of O₂, taking place separately at the anodes:



These reactions take place in two steps. That means the hydroxyle ions discharge separately one by one. At intermediate stage adsorbed hydrogen atoms (H_{ads}) are present:



where: M – surface metal atom

The adsorbed hydrogen atom can react to molecular hydrogen according to Tafel reaction (5) or Heyrovsky reaction (6). Molecular hydrogen is formed and released from an electrolyte as a gas bubble.



Alternatively, it diffuses into the bulk of material as absorbed hydrogen (H_{abs}):



The rate of hydrogen absorption can be substantially influenced by surface adsorbates called recombination poisons. The presence of poisons on steel-electrolyte interface promotes hydrogen absorption by exerting a blocking action on recombination of hydrogen. The poisons include the following elements and certain of their compounds: S, P, As, Se, Sn, Sb, Te. When hydrogen recombination is retarded, the ability of atomic hydrogen to enter steel is promoted [4,5]

MECHANISMS OF HYDROGEN DEGRADATION

The numerous mechanisms have been proposed to explain LTHA phenomena, which reflect the many ways in which hydrogen was observed to interact with metals [2,3,6].

Internal Pressure Model

Precipitation of molecular hydrogen at internal defects (nonmetallic inclusions, voids) develops high internal pressure. This pressure is added to applied stress and thus lowers the apparent fracture stress. The mechanism was initially proposed by Zapffe and Sims.

Hydrogen Induced Decohesion Model

Dissolved hydrogen (lattice hydrogen) reduces the cohesive strength of the lattice, i.e. interatomic bonds and thereby promotes decohesion. Mechanism has been proposed by Troiano and modified by Oriani. There is absence of direct experimental measurements supporting this mechanism. There are also a number of “open issues” relating to the observational base on which the decohesion model is founded. The most important is that fractography of transgranular fracture resulting from decohesion should be cleavage fracture, whereas most observations can be classified as quasi-cleavage.

Surface Energy Model (Adsorption Model)

Adsorption of hydrogen reduces the surface energy required to form a crack propagation and thus lowering of fracture stress. This model was first proposed by Petch. There are no direct experimental observation and reliable calculations that hydrogen can reduce surface energy.

Adsorption Induced Localised Slip Model

Adsorption of environmental hydrogen atoms at crack tip results in weakening of interatomic bonds facilitating dislocation injection from a crack tip and then crack growth by slip and formation of microvoids. Mechanism has been proposed by Lynch.

Hydrogen Enhanced Localised Plasticity (HELP) Model

Absorption of hydrogen and its solid solution facilitates dislocation motion or generation, or both. Mechanism first proposed by Beachem and developed by Birnbaum et al.

In many cases, the definition of hydrogen-related fracture as a “brittle fracture” is based on loss of macroscopic ductility (e.g. decrease of reduction in area and elongation). Careful fractographic examinations with high resolution technique shows, that hydrogen embrittlement of steel is associated with locally enhanced plasticity at the crack tip. Distribution of hydrogen can be highly nonuniform under an applied stress. Thus, locally the flow stress can be reduced, resulting in localised deformation that leads to highly localised failure by ductile processes, while the macroscopic deformation remains small.

In-situ transmission electron microscope (TEM) observations of deformation and fracture of samples in environmental cell gave evidence that HELP model is a viable failure mechanism for a large number of pure metals and alloys: Fe, austenitic stainless steels, Ni, Al, α -Ti alloys. The effect of hydrogen on fracture in TEM environmental cell was studied for static crack under stress. On adding hydrogen gas to the cell, dislocation sources began to operate and dislocations began to increase their velocities. Removal of hydrogen from the cell resulted in cessation of dislocation motion. This cycle could be repeated many times.

Corrosion Enhanced Plasticity (CEP) Model

This model takes into account the generation of vacancies due to localised anodic dissolution and hydrogen evolution by cathodic reaction at the freshly depassivated crack tip. Thus, corrosion produces enhanced localised plasticity. The activated dislocations along slip bands form pile-ups interacting with obstacles. The resulting high local stress can initiate cracking. Model was developed by Magnin et al. This model is applied mainly to passive metals and alloys like stainless steels, nickel and its alloys.

Hydrogen Rich Phases Model

This model implies formation of hydrogen rich phases – hydrides, whose mechanical properties differ from those of matrix. Cracking could proceed by the formation and cracking of brittle hydride near the crack tip. Model was generalised by Westlake. For iron it has been found that no stable hydrides are formed up to hydrogen pressure of 2 GPa, so this model is not valid for steel hydrogen degradation.

MATERIAL AND EXPERIMENTAL PROCEDURE

A quenched and tempered plate 12 mm in thickness made of 14HNMBCu steel grade – S690Q grade with minimum yield strength of 690 MPa according to PN-EN 10137-2 [7] was used. The chemical compositions of the tested steel is given in Table 1.

Submerged arc welded (SAW) and shielded metal arc welded (SMAW) joints were prepared. Mechanical properties obtained from a tensile test performed according to PN-EN 10002-1 [8] are presented in Table 2.

Table 1. Chemical composition of steel plate (control analyse)

Steel grade	Chemical composition, wt %												
	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	Ti	V	Al	B
14HNMCu	0.13	0.21	0.83	0.001	0.005	0.43	0.74	0.40	0.25	0.004	0.05	0.02	0.002

Table 2. Mechanical properties (transverse direction) of steel plate and its welded joints

Steel grade	Samples	Yield Strength MPa	Tensile Strength MPa	Elongation %	Reduction in Area %
14HNMCu	Base metal	908	935	8.7	47.4
	SAW	601	631	7.2	55.5
	SMAW	599	687	6.6	61.9

Microstructures of the steel plate and welded joints were examined with the use of the optical microscope LEICA MEF4M according to PN-EN 1321 [9]. Microstructure of the steels composed of low carbon tempered lath martensite. Microstructure of the welded joint was typical for extra high-strength low-alloy steel. Weld metal microstructure composed of acicular ferrite and bainite. Microstructure of regions of HAZ (coarse grained region, fine grained region, and intercritical region) consisted low carbon lath martensite with various prior austenite grains size respectively.

In order to estimate the degree of hydrogen degradation of tested steel and its welded joints, the constant load test on round notched specimens 6 mm in diameter was conducted along with PN-EN 2832 [10]. The gauge length of samples was 50 mm. The geometry of a notch is presented in Fig. 1. 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, prepared consistent with PN-66/C-06502 [11]. Tests in sea-water were conducted at open circuit potential and under cathodic polarisation with constant current densities chosen from the polarisation curves. The following cathodic currents were applied: 0.1; 1; 10 mA/cm² giving cathodic hydrogen charging of specimens during a test. Minimum two samples were used for each test parameters.

The constant load test was carried out with the use of a lever machine with leverage 25:1 and maximum load capacity of 20 kN. The machine was equipped with the environmental cell with platinum polarisation electrode (Fig. 2). Time to failure of specimen was recorded. When a sample did not fail within 200 hours, the test was finished 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 at slow strain rate 10⁻⁶ s⁻¹ in air using the same notched samples as for the constant load test.

Results of the constant load test are presented in Tables 3-5.

Fracture surfaces of failed samples were investigated with the use of the scanning electron microscope (SEM) PHILIPS XL30 to determine mode of fracture. Results of fractographic observations are shown in Fig. 3-4.

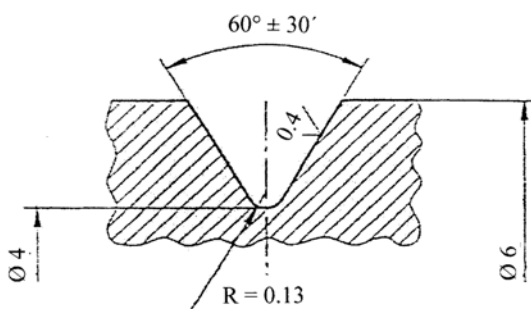


Fig. 1. The notch geometry of a specimen

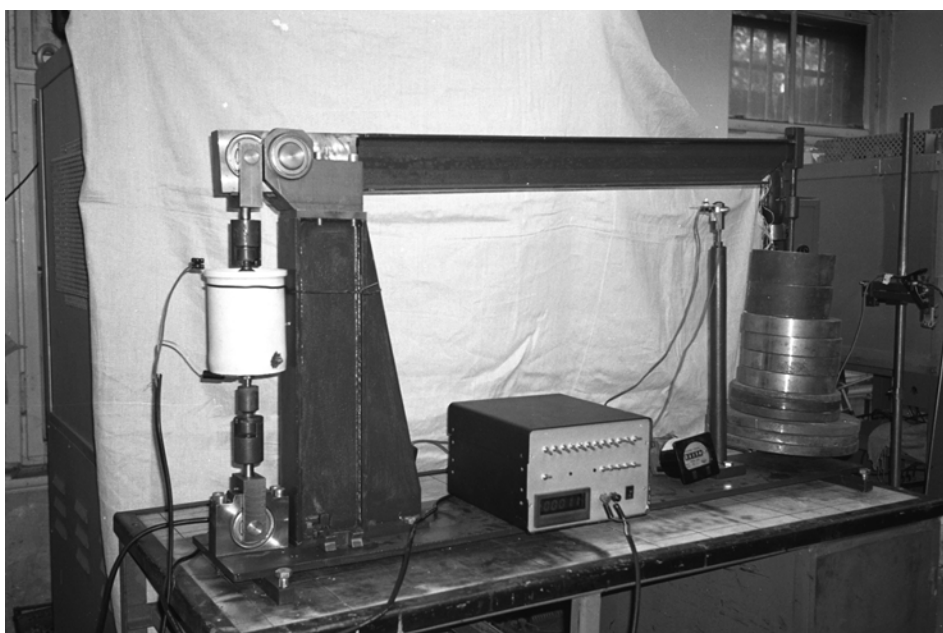


Fig. 2. View of the lever machine with the environmental cell

Table 3. Resistance to delayed hydrogen cracking of 14HNMCu 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 and resistance to delayed hydrogen cracking
 + means premature failure and susceptibility to delayed hydrogen cracking

Table 4. *Resistance to delayed hydrogen cracking of welded joints (SAW) of 14HNMCu 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 and resistance to delayed hydrogen cracking
 + means premature failure and susceptibility to delayed hydrogen cracking

Table 5. *Resistance to delayed hydrogen cracking of welded joints (SMAW) of 14HNMCu 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 and resistance to delayed hydrogen cracking
 + means premature failure and susceptibility to delayed hydrogen cracking

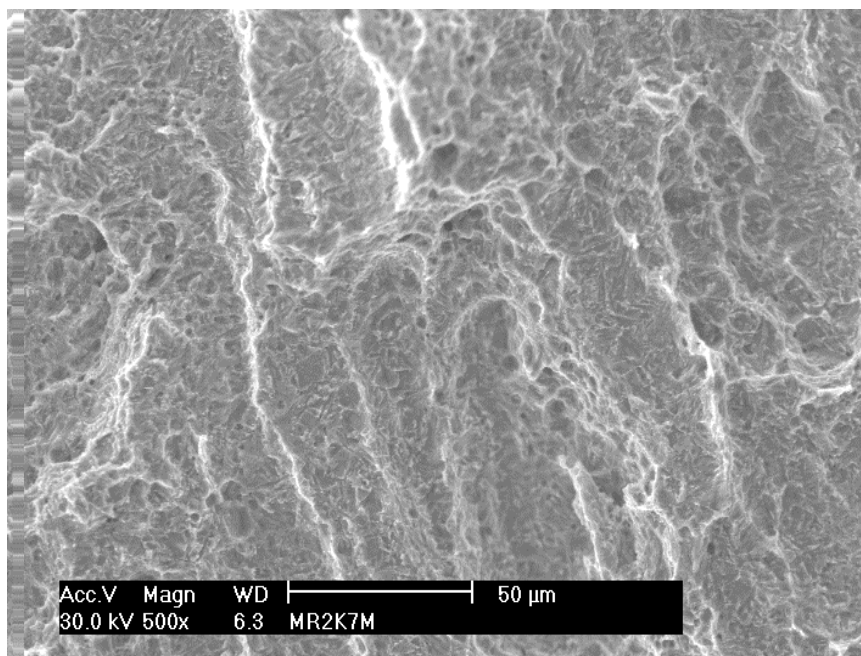


Fig. 3. SEM image of fracture surfaces of 14HNMCu steel after a constant load test in seawater. Relative load $F/F_m = 0.96$, open circuit potential

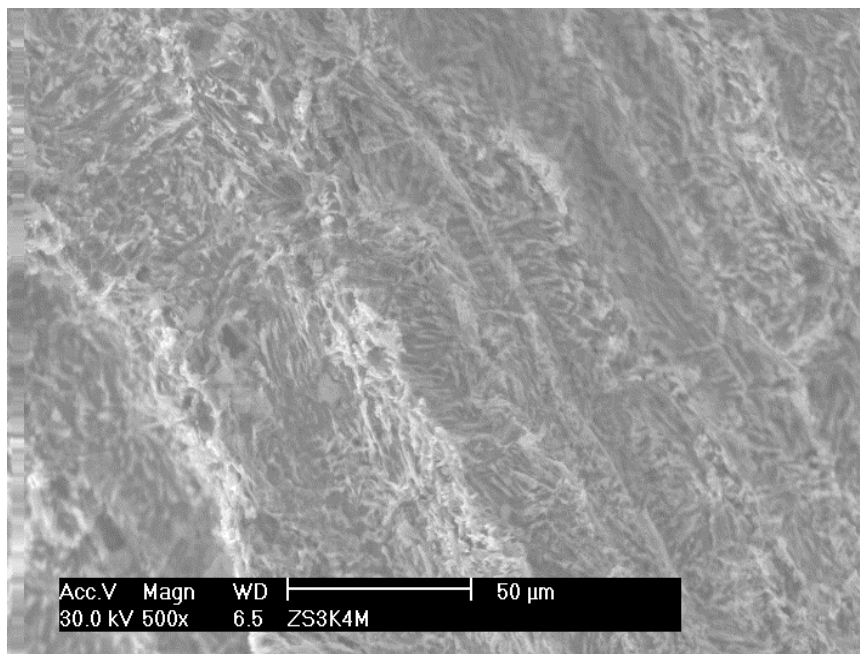


Fig. 4. SEM image of fracture surfaces of welded joint (SAW) of 14HNMCu steel after a constant load test in seawater. Relative load $F/F_m = 0.96$, open circuit potential

DISCUSSION

Tables 3-5 present critical relative loads and cathodic current densities at which delayed hydrogen cracking occurs in 14HNMCu steel and its welded joints. As it can be seen tested steel and its welded joints have high resistance to hydrogen degradation in seawater both at open circuit potential and cathodic polarisation. 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 than base metal. However, shielded metal arc welded (SMAW) joint is more susceptible than 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 result in different mechanical properties (strength, hardness) and different susceptibility to hydrogen degradation. Fractographic observations of failed samples revealed mixed fracture mode composed of ductile and quasicleavage fracture.

Obtained results of constant load test and fractographic observations suggest that hydrogen-enhanced localised plasticity (HELP) model is more applicable mechanism of hydrogen degradation than others. Hydrogen delayed cracking occurs at load level as high as flow stress (yield strength) of tested steel and its welded joints. Ductile and quasicleavage fracture modes support suggestion that hydrogen interacts with dislocations and increase their mobility, and at the same time hydrogen is transported by mobile dislocations.

CONCLUSIONS

- High-strength low-alloy steel 14HNMBCu grade S690Q and its welded joints have high resistance to hydrogen delayed cracking in seawater environment.
- Submerged arc welded joint (SAW) has higher resistance to hydrogen degradation than base metal. However, shielded metal arc welded (SMAW) joint is more susceptible than base metal.
- Under the critical load and cathodic current density the notched samples premature failed. Hydrogen-enhanced localised plasticity (HELP) model is a viable degradation mechanism.

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