

## Hydrogen degradation of high-strength steels

**J. Ćwiek\***

Division of Materials Processing Technology, Management and Computer Techniques in Materials Science, Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland

\* Corresponding author: E-mail address: janusz.cwiek@polsl.pl

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### Properties

#### ABSTRACT

**Purpose:** of this paper is to evaluate susceptibility of high-strength steels and welded joints to hydrogen degradation and to establish applicable mechanism of their hydrogen embrittlement and hydrogen delayed cracking.

**Design/methodology/approach:** High-strength quenched and tempered steel grade S690Q and its welded joints have been used. Structural low-alloy steel 34CrAlNi7-10 with various plasma nitrided layers was evaluated. Susceptibility to hydrogen embrittlement of steel, welded joints, and nitrided layers was evaluated using monotonically increasing load. Slow strain rate test (SSRT) was carried out in hydrogen generating environments. Susceptibility to hydrogen delayed cracking was evaluated under constant load in artificial sea water. Fractographic examinations with the use of a scanning electron microscope (SEM) were performed to establish suitable mechanism of hydrogen-enhanced cracking.

**Findings:** 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 than for the base metal. Tested steel and welded joints reveal high resistance to hydrogen degradation under constant load. Plasma nitrided layers are effective barriers for hydrogen entry into structural steel.

**Research limitations/implications:** There has been no possibility to perform direct observations of exact mechanism of hydrogen-assisted cracking so far. Further research should be taken to reveal the exact mechanism of increased plasticity of a nitrided layer with absorbed hydrogen.

**Practical implications:** Tested steel and its welded joints could be safely utilized within elastic range of stress in hydrogen generating environments, and constructions under cathodic protection provided that overprotection does not take place.

**Originality/value:** Hydrogen-Enhanced Localized Plasticity (HELP) model is a more applicable mechanism of hydrogen degradation than the others for high-strength steels in hydrogen generating environments. Evidences of likely increased plasticity of nitrided layers with absorbed hydrogen were observed.

**Keywords:** Crack resistance; High-strength steel; Welded joints; Hydrogen degradation

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## 1. Introduction

Synergic action of stress and environment may result in various types of degradation of metallic materials (Fig. 1). Environmentally assisted cracking (EAC) is a general term encompassing more specific terms such as: stress corrosion cracking (SCC), hydrogen embrittlement (HE) or hydrogen assisted/induced cracking (HAC/HIC), corrosion fatigue (CF), liquid metal embrittlement (LME), and solid metal induced embrittlement (SMIE). In all these cases, cracks initiate and grow at lower stresses in the presence of specific environments than in inert environments. Hydrogen has influence on three forms of EAC, i.e. hydrogen embrittlement, stress corrosion cracking, and corrosion fatigue [1].

Harmful influence of hydrogen at temperatures below 200°C is termed as low temperature hydrogen attack (LTHA). Hydrogen degrades properties of steels mainly by delayed cracking at stress below the yield strength – hydrogen stress cracking (HSC), 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) [2].

Hydrogen effect is greater near room temperature and decreases with increasing strain rate. Hydrogen degradation is more pronounced with increasing hydrogen content or a charging rate [3].

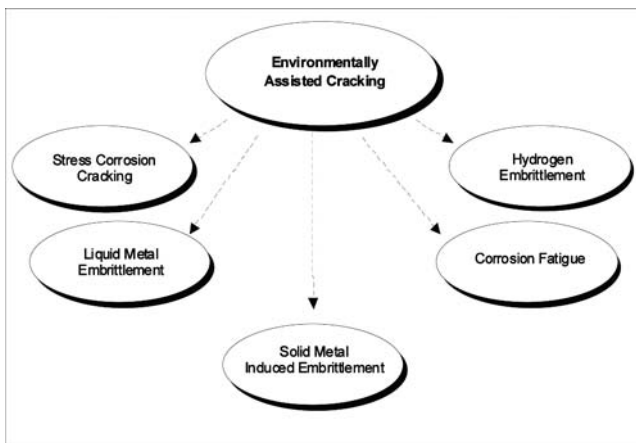


Fig. 1. Forms of environmentally assisted cracking

The susceptibility of steel to hydrogen degradation is influenced by a strength level and microstructure of steel. Steels with tensile strength less than 700 MPa appear to be resistant to hydrogen cracking, and structures made of 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 [3, 4].

Hydrogen degradation is still a serious problem in many industry branches because it leads to dangerous failures as well as to loss of property. These industry branches are as follows: chemical (ammonia, cyanides), refinery (catalytic crackers, storage tanks), power plants (boilers, turbines), marine structures, long distance sour gas transportation pipeline, car and aircraft components [1, 2]

Hydrogen embrittlement was a cause of failures in high-strength structural steels used in the offshore industry. The problem is due to absorption of hydrogen from seawater, which is promoted when cathodic protection is applied for steel to control corrosion. Hydrogen induced cracking is still a common problem in fabrication of constructions in a form of welds cold cracking [5-7].

A number of failures due to hydrogen was reported for car and ship engines parts. Engine oil can absorb moisture and become acidic, so that hydrogen could be generated at crack tip and facilitate crack growth [1, 2].

## 2. High-strength steels

High-strength low-alloy (HSLA) steels have been widely used in constructions of large scale welded-structures. The principal advantage of these steels is a good combination of strength and toughness, but also their good weldability. Therefore HSLA steels are suitable to be applied for

- 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.

HSLA steels are produced as: quenched and tempered, directly 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 extra use could be their hydrogen degradation.

Medium carbon steels (plane carbon and alloyed steels) with carbon content from 0.25 to 0.55% are widely used for machine, car and airplane parts. Alloy steels are utilised in quenched and tempered condition [4, 8].

## 3. The role of microstructure in hydrogen degradation

With respect to microstructure of ferritic steels, susceptibility to hydrogen degradation increases successively for structures: spheroidized (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 spheroidized structures) are more resistant than coarser and more angular ones (pearlite). However, a coarse spheroidized structure was found to be more susceptible to hydrogen degradation than less tempered structure or fine-grained normalised structure [2].

Hydrogen degrades properties of steel provided where cracking proceeds by all microstructural modes, including: ductile fracture, quasi-cleavage, transgranular cleavage, and brittle intergranular fracture [9].

## 4. Hydrogen in metals

Hydrogen is the most abundant element in the universe, is safe and clean fuel gas of high calorific value, available in unlimited quantities by the electrolysis of water. Non-polluting, it produces essentially only water from which it was originally derived as a combustion product, and from which it may be recovered for re-use.

Many of the hydrogen-powered motor vehicles having been developed so far utilise the ability of some metals and alloys to react reversibly with hydrogen to form metal hydrides, enabling low-pressure, but high storage density. It is possible, by careful selection of the metallic components of hydride, to store slightly greater volume of hydrogen as hydride than as liquid hydrogen, and about a magnitude more than as compressed gas.

This method of storage almost completely eliminates dangers of high pressure hydrogen gas storage and its obvious problems about heavy containment vessels, as well as the probability of fire or explosion if containment integrity is violated in an accident.

Hydrogen is the lightest element with an atomic structure of one proton and a single electron and is, in its natural state, a diatomic molecular gas, H<sub>2</sub>. The diatomic hydrogen molecule is too large to enter the surface of a solid metal, and must be dissociated into single atoms to readily cross the gas/metal interface. Two mechanisms for this are known, electrochemical and chemisorption. If the metal is molten, molecular hydrogen can dissolve readily, but dissociates once in solution and can be retained as a mono-atomic solute on solidification.

The electrochemical evolution of atomic hydrogen is part of the cathode reaction in either a corrosion cell or an electroplating process. In addition, these can include such processes as acid cleaning and cathodic protection systems. As corrosion is essentially an electrochemical mechanism, both are sufficiently similar to be considered identical for the purpose of hydrogen evolution, and take the form of:



Most of hydrogen atoms thus formed quickly combines to form diatomic gaseous hydrogen, but a portion of it enter the metal surface and remain as individual atoms in solution.

Chemisorption dissociation of hydrogen is a rather different mechanism. As a hydrogen molecule approaches a metal surface, weak van Der Waal's forces begin to act upon it, drawing it closer. An interstitial solute, hydrogen remains in the mono-atomic form and is relatively mobile, even at ambient temperatures. However, to maintain such a mobile atom as an interstitial solute presents problems in metals, although crystallines are far from being

perfect, and lattice defects present areas where the lattice strain induced by the solute hydrogen atom is reduced, and thus will act as hydrogen traps.

If the trap site is a vacancy, the presence of a single hydrogen atom will lower the lattice strain due to the vacancy, and the hydrogen atom becomes a substitutional, rather than an interstitial solute.

If the trap is a line defect, there may well accumulate a string of hydrogen atoms along the defect. The presence of a string of individual hydrogen atoms would not immobilise a dislocation, although it would increase the applied stress needed for movement.

However, if two adjacent atoms on a line defect recombine to form molecular hydrogen, the applied stress required to cause movement becomes much greater, effectively pinning the dislocation at that point.

Since dislocation movement is the underlying process to plastic flow, the ductility of the material is reduced and the probability of brittle failure increased by the presence of hydrogen. In this context, interfaces such as grain boundaries or second phases should be considered as dislocation arrays, and thus are likely to accumulate solute hydrogen, quite possibly in molecular form, embrittling the interface [10-12].

In addition to reducing the mobility of dislocations, solute hydrogen can also react, either with the solvent metal to form a hydride, or with some other solute element to form a new phase. Iron at normal pressures and temperatures does not form hydrides. Hydrogen attacks ferritic steels by two distinct and different mechanisms. One at ambient temperature is known as "hydrogen embrittlement" or low temperature hydrogen attack. The other is a high temperature phenomenon, at the temperature above 200°C, known as "high temperature hydrogen attack" [2].

## 5. Low temperature hydrogen attack

Hydrogen included damage describes any of a number of forms of degradation of metals caused by exposure to environments (liquid or gas) which cause absorption of hydrogen into the material to cause degradation in mechanical performance.

Examples of hydrogen induced damage are:

- Formation of internal cracks, blisters or voids in steels.
- Embrittlement (i.e. loss of ductility).

A component or structure can be contaminated by hydrogen in various stages of its life. This begins in the metallurgical process, because the hydrogen solubility in the molten metal is much higher than in the solid condition (Fig. 2). This hydrogen loading is reversible to a great extent, because it is caused mainly by the storage of the hydrogen in the interstitial positions of the lattice. Irreversible hydrogen degradation only occurs if the hydrogen can effuse or if it can accumulate as gas in the hollow spaces. This type of hydrogen damage is of importance in welding practice in the form of cold cracks. This type of damage is also produced during casting as fish eyes (or fakes) [2, 13].

Hydrogen embrittlement is described as a three-step process. Firstly, hydrogen is introduced into the metal, via electrochemical charging or via gaseous absorption. In some cases, hydrogen may be introduced in the lattice prior to stressing (e.g. during fabrication). This situation is commonly referred to as internal

hydrogen embrittlement. Secondly, atomic hydrogen is transported through the metal lattice, increasing its concentration in the tensile-stressed surroundings of the crack tip due to gradients in the chemical-potential. In the absence of a crack, atomic hydrogen may be transported to an initiation location. Thirdly, the combined action of stress and hydrogen concentration leads to failure of the metal in an embrittled zone [14].

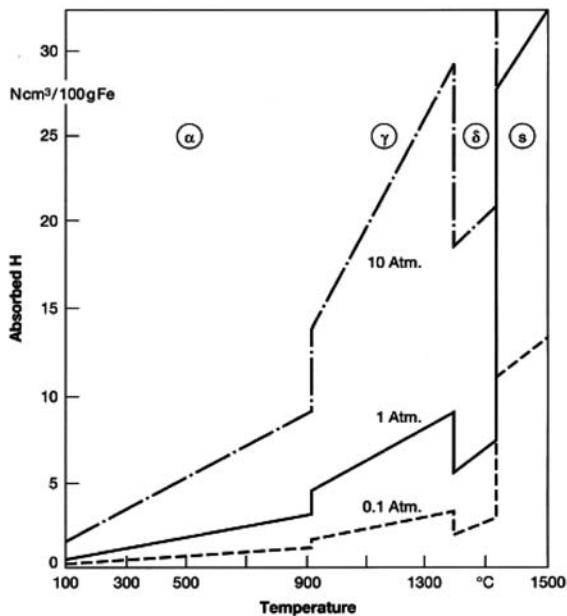


Fig. 2. Solubility of hydrogen in iron as a function of temperature and pressure [2, 13]

When hydrogen enters material it can affect the mechanical performance of materials in several ways [1, 2, 4]:

1. The formation of internal hydrogen blisters or blister-like cracks at internal delaminations or at sites of non-metallic inclusions in low strength materials. These internal cracks may propagate by a process called hydrogen-induced cracking (HIC) or hydrogen blistering. No external stress is usually required to induce this type of cracking. In some cases, however, these blister cracks may take on an alignment caused by the presence of residual or applied tensile stresses.
2. The loss of ductility in a tensile test as reflected by a decreased reduction in area which is generally called hydrogen embrittlement (HE). The process of hydrogen-assisted microvoid coalesce can occur during plastic straining. This can reduce the ductility of normally ductile engineering materials while not inducing brittle cracking.
3. Delayed cracking at stress below the yield strength – hydrogen stress cracking (HSC)
4. An extreme case of ductility loss from hydrogen is the brittle fracture of susceptible materials under applied or residual tensile stresses. This form of cracking, which typically changes from transgranular to intergranular with increasing yield strength and other processing variables, is normally referred to as hydrogen embrittlement cracking (HEC).

5. Brittle failure by cracking under the combined action of tensile stress and corrosion in the presence of water and hydrogen sulphide - sulphide stress corrosion cracking (SSCC).

With respect to HE and HEC, 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 relative short time (i.e., <1000 h). Therefore, tension, notched, and precracked specimens and fracture methods are widely utilized in the evaluation for HEC.

## 6. High temperature hydrogen attack

High temperature hydrogen attack is a surface decarburization and chemical reaction with hydrogen. Hydrogen attack, unlike hydrogen embrittlement, involves the formation of the second phase by the solute hydrogen, and, unlike the previous mechanisms, is an elevated temperature phenomenon. Hydrogen solubility in  $\alpha$ -Fe is negligible. Similarly, the solubility of carbon in  $\alpha$ -Fe is extremely small. However, if the two are present they can react together, at a suitable elevated temperature, to form methane.



The reaction occurs at grain boundaries, where the methane gas exerts internal pressure and forms fissures or elongated pores on metal. This phenomenon was observed in the petrochemical and synthetic ammonia industries, where items of equipment spend substantial periods of time, years rather than hours, at high temperatures and in contact with hydrogen. Thus, they can be considered to operate in equilibrium conditions in microstructural and metallurgical thermodynamics aspects. While in contact with hydrogen containing process streams in such plants, the hydrogen is normally either molecular or combined with carbon, and the electrochemical processes responsible for the mono-atomic hydrogen causing hydrogen embrittlement are absent because of the lack of water in the process stream. However, the previously discussed chemisorption mechanism can provide a source of individual hydrogen atoms at a metal surface in the absence of an aqueous electrochemical mechanism.

The material appears at a macro-scale to become decarburised, and this is the initial indication of hydrogen attack when normal macro scale examination techniques are employed. As the supply of hydrogen continues, an increasing amount of methane is formed, consuming more and more carbon. The methane molecule is large, and is immobile in the lattice, and voids are formed in microstructure. It is believed that these voids grow initially by the diffusion of iron atoms away from the void that is essentially a vacancy condensation mechanism. After reaching a critical size, growth is by power-law creep driven by the increasing methane pressure within the void.

The behaviour of the more common engineering steels in a hydrogen environment was summarised by Nelson, who examined data from many operating hydrocarbon processing plants around the world, and produced a family of curves, known as the "Nelson Curves" [2, 10].

## 7. Hydrogen entry into metals

Hydrogen can be introduced into metals and alloys in certain environments and there are numerous ways for hydrogen to enter metals. Among these, there is exposure to hydrogen gas and electrolytic deposition of hydrogen on metal electrodes. The electrolytic process is a very effective way of introducing hydrogen since it can sustain high equivalent pressure of hydrogen gas at metal surface.

### 7.1. Gas phase

Initial studies of the solubility of hydrogen in iron and other metals can be attributed to Sieverts et al. who found experimentally that amounts of hydrogen dissolved in metal can be directly proportional to the square root of the hydrogen pressure  $P$ , and the equilibrium can be written as [15]:



Thus the solubility of hydrogen  $C$  in metal is:

$$C = k\sqrt{P_{H_2}} \quad (4)$$

### 7.2. Electrochemical processes in aqueous solution

In the case of hydrogen evolution and entry into metals in aqueous solution, many investigators found that amounts of dissolved hydrogen in iron and its alloys can be directly proportional to the square root of the cathodic charging current density. The mechanism of hydrogen evolution and entry into metal involves coupled discharge–chemical absorption.

Hydrogen is evolved in a mono-atomic form as part of the cathode reaction of almost any electrochemical reaction; several of them are commonly applied to ferrous surfaces. Common examples are processes such as electroplating and acid pickling, both of which are almost notorious causes of post-processing failure through hydrogen embrittlement.

Another, less obvious, electrochemical mechanism is almost any aqueous corrosion process. In most instances, the level of hydrogen generated is insufficient to give problems, and the affected layer is removed by the corrosion process itself before any damage can be done by the evolved hydrogen, but the ability of corrosion to utilise hydrogen in its destructive workings should never be underestimated.

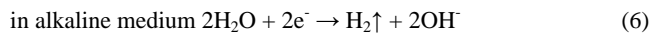
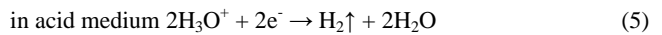
It is widely believed that hydrogen plays a major role in the mechanism of stress corrosion cracking, which is a well-known destroyer of chemical process plant and other metallic structures. Another, perhaps better understood mechanism is that of hydrogen embrittlement resulting from imposition of electrical cathodic protection systems to steel structures either buried in the ground or immersed in water. The cathodic protection technique utilises externally applied electrical charges to force the surface to be protected to become cathodic to either an inert or consumable

anode, thus protecting the surface from metal loss through corrosion. Unfortunately, the cathodic reaction includes the evolution of hydrogen which is, initially at least, in the mono-atomic form in which it can readily enter the metal surface [10].

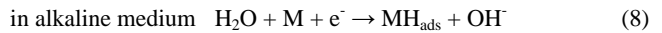
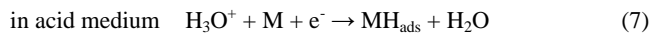
## 8. Sources of hydrogen in steel

The sources of hydrogen in steel are the following: gaseous hydrogen, liberation of atomic hydrogen by the iron-water or iron- $H_2S$  reactions, decomposition of water molecules, electrolytic and corrosion processes including a cathodic reaction.

During pickling in mineral acids, cathodic electrolytic cleaning, cathodic polarisation protection, and zinc or cadmium plating hydrogen is formed. In all cases due to a cathodic reduction. The anodic counter reaction in case of pickling is dissolution of metal and takes place at the same location as evolution of hydrogen. In case of electrolytic cleaning, cathodic polarisation or electrolytic plating, the counter reaction is the formation of  $O_2$ , taking place separately at the anodes:



These reactions take place in two steps. That means the hydroxyl ions are discharged 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 (9) or Heyrovsky reaction (10). Molecular hydrogen is formed and released from an electrolyte as a gas bubble.



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



The rate of hydrogen absorption can be greatly 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 compounds of theirs: S, P, As, Se, Sn, Sb, Te. When hydrogen recombination is retarded, the ability of atomic hydrogen to enter steel is promoted [16, 17].

Corrosion of marine constructions is prevented by coatings and cathodic protection. The later may be harmful for steels resulting in their hydrogen embrittlement. Steel could be charged



with hydrogen in the vicinity of polarisation anode, i.e. over-protection, or by presence of some sulphate-reducing bacteria in sea-water [18].

Sulphate Reducing Bacteria or “desulfovibrio” bacteria (SRB), a heterogeneous group of anaerobic heterotrophic bacteria, which use inorganic sulphate as a final electron acceptor in respiration, are the main bacteria responsible for the numerous microbiologically influenced corrosion (MIC) cases. Hydrogen sulphide as a result of the anaerobic activity of SRB reacts with iron and creates  $H_2$ :



Additionally, enlarged hydrogen absorption, with SRB presence, is due to promoting action of  $H_2S$  near material surface [17].

## 9. Hydrogen in welding

Hydrogen pick-up during fusion welding operations is a relatively straight-forward mechanism in which hydrogen, dissociated from water presented as contaminant either in welding consumables, filler materials, fluxes or shield gases, enters the molten weld pool. Alternatively, hydrogen from surface contamination of water or hydrocarbon oils or greases on the faying surfaces is absorbed into the molten weld pool and remains trapped on solidification. While the weld area remains hot from the welding process, this hydrogen diffuses away from the weld fusion zone and into the adjacent parent material. This area of parent material is the zone affected by the welding heat and is known as the heat affected zone (HAZ), and it is the area, in which transformation of the microstructure will occur due to the heating and cooling of the weld cycle. Harder transformation products are produced, and additionally the stresses generated by the contraction of the solidifying weld pool must also be accommodated. Thus there exists a region which is high in hardness, due to the metallurgical transformations resulting from the weld heat cycle, and which is subjected to a relatively high tensile load imposed by the contracting weld fusion zone. Also the ductility is locally impaired by the presence of hydrogen. The result is inevitable, and cracking occurs, usually within a few hours of the welding operation completion. Most welding codes insist that non-destructive testing of welded fabrications is delayed by at least 72 hours to allow hydrogen cracking to develop and so, not go undetected. Fortunately, in a well designed welded joint all three factors can be eliminated. Undesirable transformations of the parent material in the HAZ to unwanted hard structures are controlled by suitable preheat and controlled post-weld cooling, and any remaining unwanted transformed structures are further modified to an acceptable form by post weld heat treatment. The very presence of hydrogen is eliminated, as far as possible by elimination of hydrogen-containing water or hydrocarbons from the joint and the weld consumables, and the stresses imposed by solidification contraction are removed by post-weld stress relief. Any remaining hydrogen is also eliminated by the post-weld stress relief heat treatment [10].

## 10. Mechanisms of hydrogen degradation of metals

The numerous mechanisms were proposed to explain LTHA phenomena, which reflect the many ways in which hydrogen was observed to interact with metals [2, 9, 11, 19, 20, 21].

### 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 proposed by Troiano and modified by Oriani. There is absence of direct experimental measurements supporting this mechanism. There is also a number of “open issues” relating to the observational based 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 crack propagation and thus lowering of fracture stress. This model was first proposed by Petch. There is 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 (Fig. 3). Mechanism proposed by Lynch.

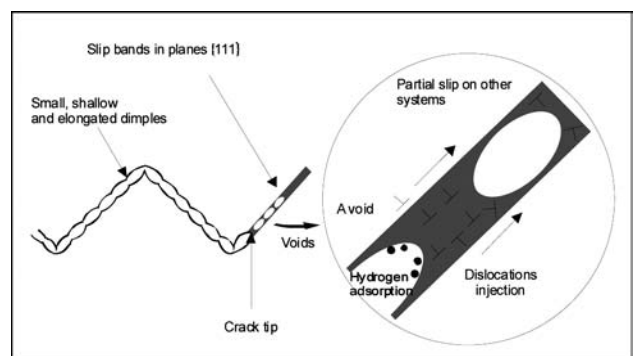


Fig. 3. Diagram illustrating the adsorption-induced localized slip process occurring along alternate shear planes [19]

**Hydrogen Enhanced Localized Plasticity (HELP) Model**

Absorption of hydrogen and its solid solution increases the ease of 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). But careful fractographic examinations with high resolution technique show that hydrogen embrittlement of steel is associated with locally enhanced plasticity at the crack tip. Distribution of hydrogen can be highly non-uniform under an applied stress. Thus, locally the flow stress can be reduced, resulting in localized deformation that leads to highly localized failure by ductile processes, while the macroscopic deformation remains low.

The mechanism of hydrogen enhanced localized plasticity (HELP) appears to be a viable one of the many suggestions for an explanation of the hydrogen related failures, Arguments in support of the HELP mechanism are based on experimental observations and theoretical calculations. The presence of hydrogen in solid solution decreases the barriers to dislocation motion, thereby increasing the amount of deformation that occurs in a localized region adjacent to the fracture surface. The fracture process is a highly localized ductile rupture process rather than embrittlement.

High-resolution fractography of hydrogen embrittled metals, such as Ni and Fe, show extensive plastic deformation localized along the fracture surfaces. 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. 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 can be repeated many times.

Principle in the HELP mechanism is the shielding of the elastic interactions between dislocations and obstacles by the hydrogen solutes. Reduction of the interaction energies between elastic stress centres results in enhanced dislocation mobility. This phenomenon is supported by strong experimental evidence and was observed in fcc, bcc, and hcp systems. As a consequence, the intrinsic material flow stress varies with position in an inhomogeneous distribution of hydrogen and is lower where the hydrogen concentration is greater.

The critical question though that still remains unanswered is how this hydrogen induced material softening at the microscale can cause shear localization at the macroscale. As Birnbaum et al. discuss, it is clear that the flow stress in the region of localization is reduced relatively to the flow stress in the homogeneously deforming volume, but the mechanism by which hydrogen causes shear localization has not been established as yet [9, 20].

**Corrosion Enhanced Plasticity (CEP) Model**

This model takes into account the generation of vacancies due to localized anodic dissolution and hydrogen evolution by cathodic reaction at the newly depassivated crack tip. Thus, corrosion produces an enhanced localized plasticity. The activated dislocations along slip bands form pile-ups interacting with obstacles. The resulting high local stress can initiate cracking (Fig. 4). Model was developed by Magnin et al. This model has

application mainly to passive metals and alloys like stainless steels, nickel and its alloys [21].

**Hydrogen Rich Phases Model**

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 generalized by Westlake. For iron it was found that no stable hydrides are formed up to hydrogen pressure of 2 GPa, so this model is not valid for steel hydrogen degradation.

Summary of possible corrosion-deformation interactions that could produce hydrogen assisted cracking is shown in Fig. 5 [19].

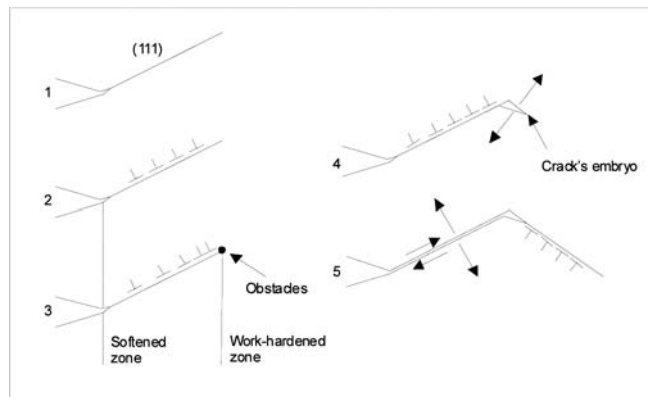


Fig. 4. Steps of the Corrosion Enhanced Plasticity Model [21]

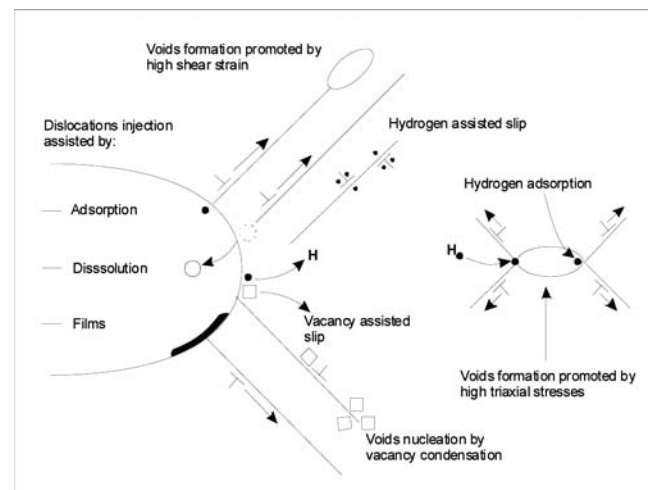


Fig. 5. Processes that could result in hydrogen assisted cracking by localized slip and microvoids coalescence [19]

**11. Prevention or remedial action**

In order to produce preventative measures, both the source of the hydrogen and the embrittlement mechanism must be known at

least approximately. As important measures in the prevention of hydrogen damage, the following points can be mentioned [2]:

- material - selection of suitable material,
- medium (environment) - it is not easy to influence, possibly by the addition of inhibitors,
- design - avoid notches, slots and sharp transitions, avoid local plastic deformation.

Base solutions to various hydrogen attack forms are as follows:

1. internal cracking or blistering
  - use of steel with low levels of impurities (i.e. sulphur and phosphorus).
  - modifying environment to reduce hydrogen charging.
  - use of surface coatings and effective inhibitors.
2. hydrogen embrittlement
  - use of lower strength (hardness) or high resistance alloys.
  - careful selection of materials of construction and plating systems.
  - heat treatment to remove absorbed hydrogen.
3. high temperature hydrogen attack
  - selection of material (for steels, use of low and high alloy Cr-Mo steels; selected Cu alloys; non-ferrous alloys).
  - limit temperature and partial pressure H<sub>2</sub> (using of the Nelson Curves).

In steels with electrolytic zinc layers, the diffusible hydrogen should be forced out during the heat treatment between 190 and 220°C because the effusion rate is far too low at room temperature (hydrogen diffusion ability in zinc layers is low).

## 12. Evaluation of susceptibility to hydrogen embrittlement

High-strength quenched and tempered steel grade S690Q and its welded joints was used. Susceptibility to hydrogen degradation of steel and welded joints was evaluated using monotonically increasing load. Slow strain rate test (SSRT) was carried out on round smooth specimens in the air, and seawater under cathodic polarization. Elongation and reduction in area were chosen as measures of susceptibility to hydrogen embrittlement. Fractographic examinations with the use of scanning electron microscope (SEM) were performed to establish suitable mechanism of hydrogen-enhanced cracking of the welded joints [22, 23].

### 12.1. Materials and experimental procedure

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

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
S690Q	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

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 are presented in Table 2.

Microstructures of the steel plate and welded joints were examined with the use of the optical microscope. Microstructure of the steels composed of low carbon tempered lath martensite. Microstructure of the welded joint was typical for high-strength low-alloy steels. 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, slow strain rate test (SSRT) according to PN-EN ISO 7539-7 was conducted on round smooth specimens 4 mm in diameter made according to PN-EN ISO 7539-4. The gauge length was 50 mm.

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. The applied strain rate was 10<sup>-6</sup> s<sup>-1</sup>. Tests in sea-water were conducted at open circuit potential and under cathodic polarisation with constant current densities, chosen from the polarisation curves obtained in artificial sea-water for base metals with the potentiostatic method. The following cathodic currents were applied: 0.1; 1; 10; 20 and 50 mA/cm<sup>2</sup>.

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 the air to that measured in artificial sea-water were calculated and presented as bar charts (Figs. 6-9).

Fracture surfaces of failed samples were investigated with the use of the scanning electron microscope (SEM) to determine mode of fracture. Examples of fractographic observations are shown in Figs. 12-16.

### 12.2. Description of achieved results

Observed decrease of relative values of elongation, and reduction in area with increase of current density exhibits a certain minimum. Further increase of current density does not cause higher degradation. The loss of elongation was as high as 45% for base metal, and 55% for welded joints. Reduction in area decreased of 90% for base metal, and 90% and 85% in the case of SMAW and SAW welded joints respectively. Changing of relative fracture energy with increase of current density is similar to shifting relative elongation. Tensile strength is at constant level which is typical for hydrogen embrittlement phenomenon.



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 %
S690Q	Base metal	908	935	8.7	47.4
	SAW	601	631	7.2	55.5
	SMAW	599	687	6.6	61.9

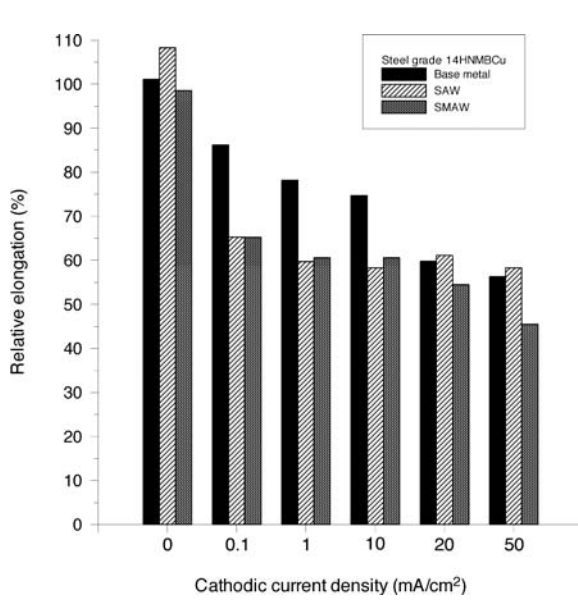


Fig. 6. Relative elongation versus cathodic current density for 14HNMCu steel and its welded joints

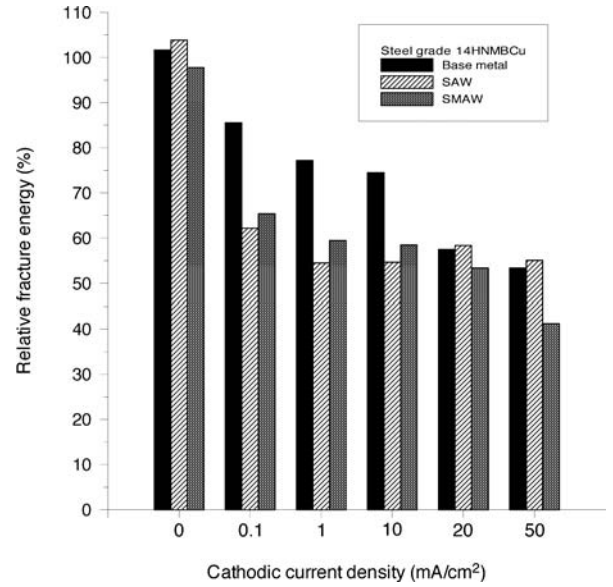


Fig. 8. Relative fracture energy versus cathodic current density for 14HNMCu steel and its welded joints

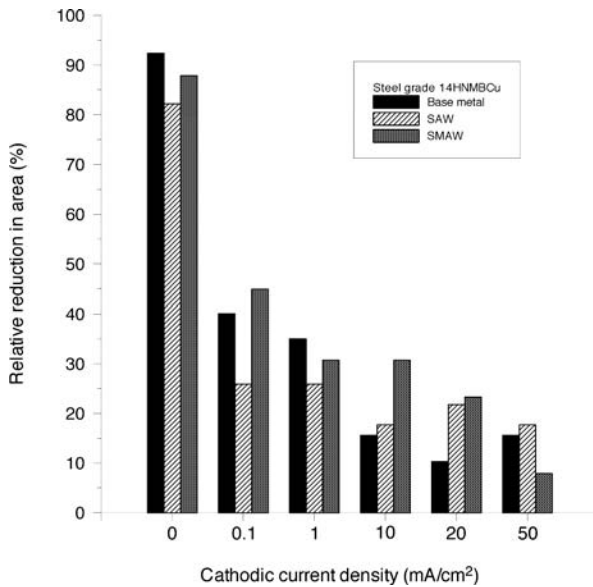


Fig. 7. Relative reduction in area versus cathodic current density for 14HNMCu steel and its welded joints

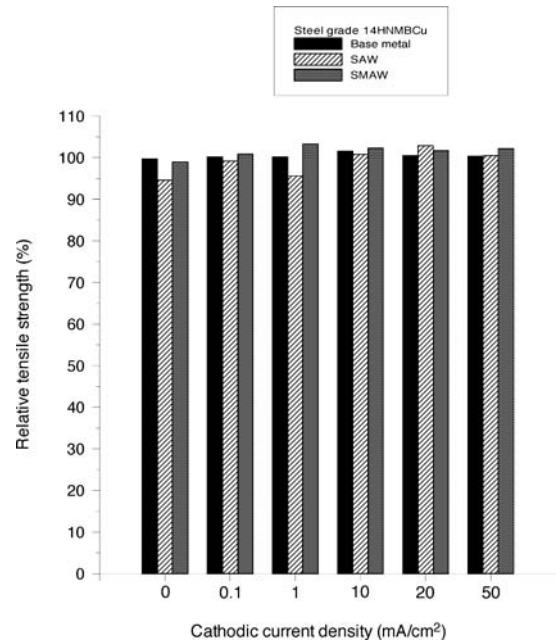


Fig. 9. Relative tensile strength versus cathodic current density for 14HNMCu steel and its welded joints

Failure of samples with welded joints occurred always in weld metal (Figs. 10-11), 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 the air, crack growth occurred in a ductile mode. Base metal samples tested in the air had mixed-quasi-cleavage and micro void coalescence (MVC) fracture (Fig. 12). Under cathodic polarisation base metal changed fracture mode, i.e. portion of quasi-cleavage fracture increased (Fig. 13), and cleavage fracture also appeared at higher current densities. Samples with welded joints tested in the air revealed ductile – MVC fracture mode (Fig. 14). When cathodic polarization was applied, mixed – MVC and quasi-cleavage fracture was observed (Fig. 15). At higher cathodic current densities, the presence of hydrogen induced microcracks and flakes in weld metal (Fig. 16).

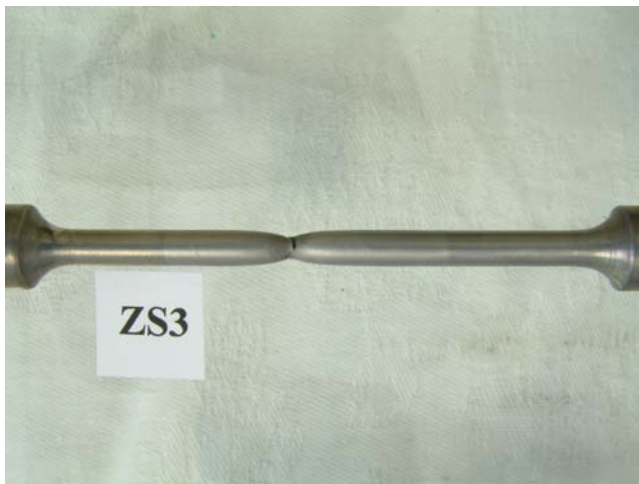


Fig. 10. View of the sample with SAW welded joint after SSRT in the air. Fracture localized in weld metal

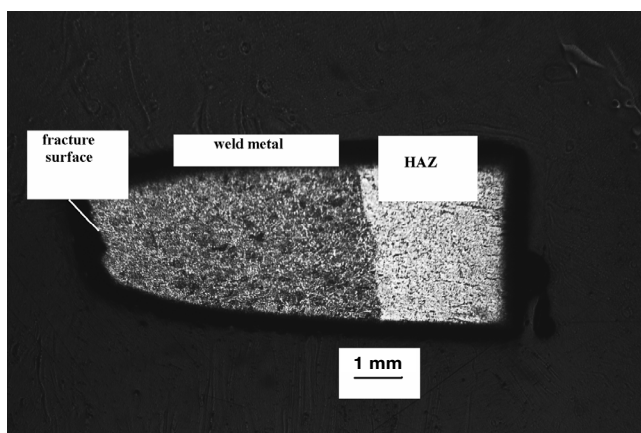


Fig. 11. Longitudinal cross section of the sample with SAW welded joint after SSRT in the air. Fracture localized in weld metal. Etched with 4%  $\text{HNO}_3$

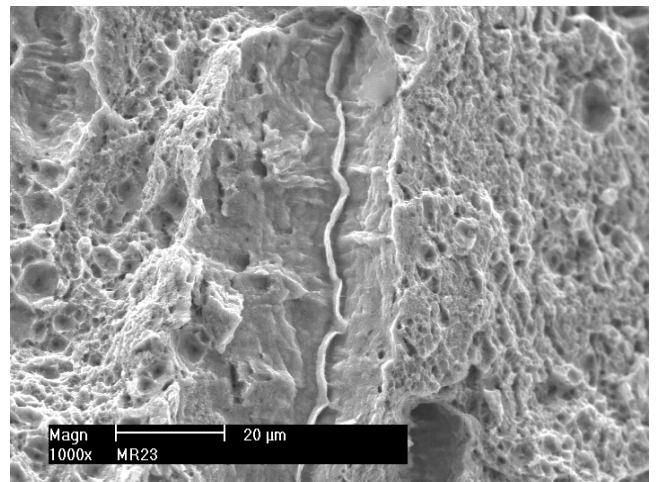


Fig. 12. SEM image of fracture surface of base metal sample after SSRT test the air

Obtained results of SSRT test and fractographic observations suggest that hydrogen-enhanced localised 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. 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 facilitates cracking.

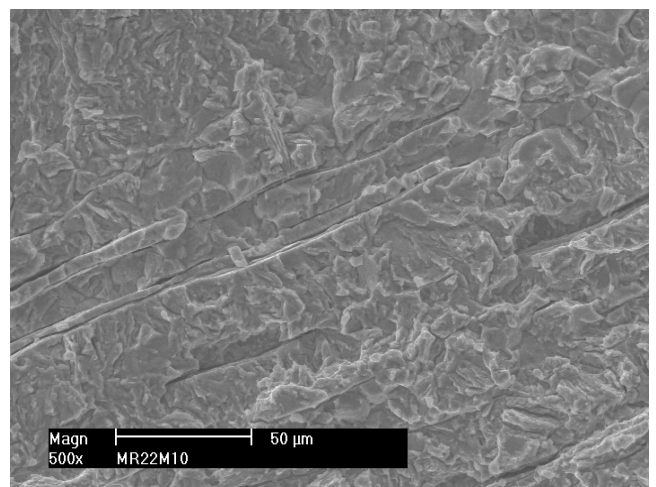


Fig. 13. SEM image of fracture surface of base metal sample after SSRT test in seawater,  $i = 10 \text{ mA/cm}^2$



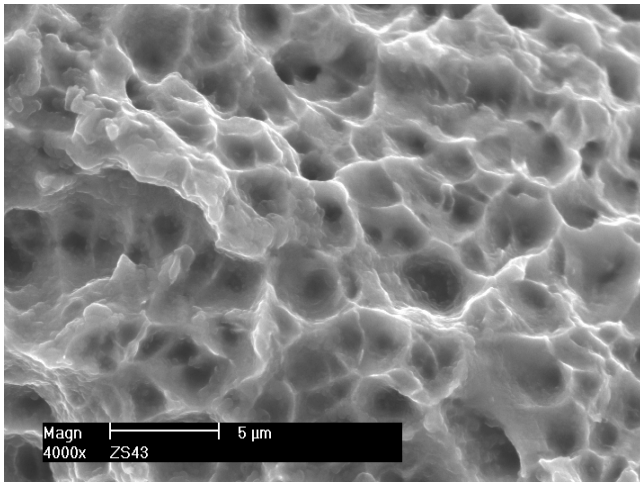


Fig. 14. SEM image of fracture surface of sample with SMAW welded joint after SSRT test in the air. Fracture localized in weld metal

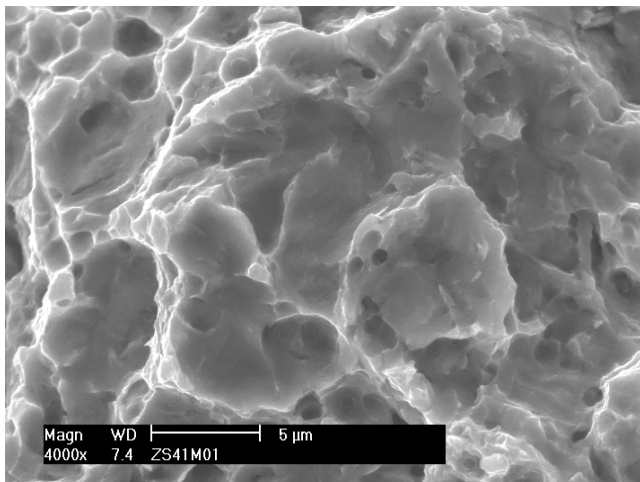


Fig. 15. SEM image of fracture surface of sample with SMAW welded joint after SSRT test in seawater,  $i = 0.1 \text{ mA/cm}^2$ . Fracture localized in weld metal

### 13. Evaluation of susceptibility to hydrogen delayed cracking

High-strength quenched and tempered steel grade S690Q and its welded joints were used. A quenched and tempered plate 12 mm in thickness made of S690Q steel grade with minimum yield strength of 690 MPa according to PN-EN 10137-2 was used. The chemical compositions of the tested steel are given in Table 1.

Submerged arc welded (SAW) and shielded metal arc welded (SMAW) joints were prepared. Mechanical properties obtained from the tensile test performed according to PN-EN 10002-1 are presented in Table 2 [24].

Susceptibility to hydrogen delayed cracking was evaluated under constant load in hydrogen generating environment. Test were carried out using round notched specimens subjected to axial tensile load being equivalent to 75-96% of maximum force obtained from tensile tests in the air. Specimens with and without welded joint were investigated in sea-water under cathodic polarization at room temperature. Presence or lack of cracking within 200 hours was chosen as a measure of susceptibility to hydrogen delayed cracking. Fracture modes of failed samples were examined with the use of scanning electron microscope.

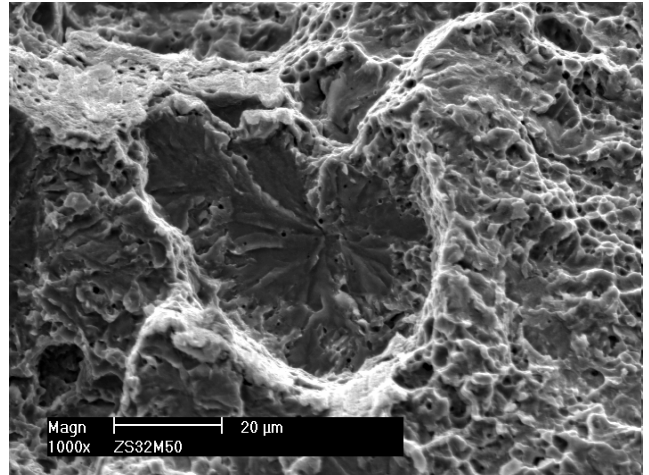


Fig. 16. SEM image of fracture surface of sample with SAW welded joint after SSRT test in seawater,  $i = 50 \text{ mA/cm}^2$ . Fracture localized in weld metal

#### 13.1. Materials and experimental procedure

In order to estimate the degree of susceptibility to hydrogen delayed cracking (hydrogen stress cracking) of tested steel and the welded joints, the constant load test on round notched specimens 6 mm in diameter was conducted along with PN-EN 2832. The gauge length of samples was 50 mm. The geometry of a notch is presented in Fig. 17. For samples with welded joints, welds were placed in the centre of specimens and a notch was cut in the fusion line, so the axis of a notch crossed both weld metal and HAZ. All specimens were cut along the transverse direction. 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. 18).

Tests were performed at room temperature in standard artificial sea-water grade A, prepared consistent with PN-66/C-06502. 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/cm<sup>2</sup> giving cathodic hydrogen charging of specimens during a test.

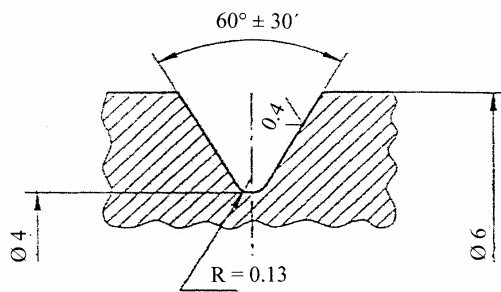


Fig. 17. The notch geometry of a specimen



Fig. 18. View of the lever machine with the environmental cell

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 prematurely (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 the tensile test. The tensile test was performed at slow strain rate  $10^{-6} \text{ s}^{-1}$  in the air using the same notched samples as for a constant load test.

Table 3.  
Resistance to delayed hydrogen cracking of S690Q steel under constant load test in sea water

Cathodic current density $\text{mA/cm}^2$	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

### 13.2. Description of achieved results

Results of the constant load tests in hydrogen generating environments are presented in Tables 3-5.

Table 4.  
Resistance to delayed hydrogen cracking of welded joints (SAW) of S690Q steel under a constant load test in sea water

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

Table 5.  
Resistance to delayed hydrogen cracking of welded joints (SMAW) of S690Q steel under a constant load test in sea water

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

Fracture surfaces of failed samples were investigated with the use of the scanning electron microscope (SEM) PHILIPS XL30 to determine mode of fracture. Examples of fractographic observations are shown in Figs. 19-22.

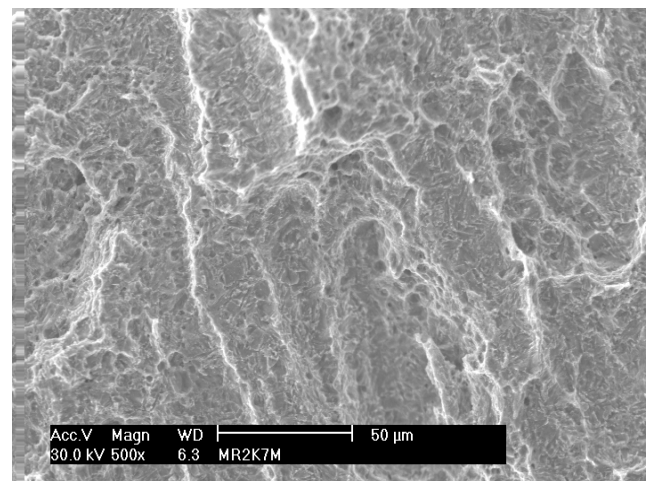


Fig. 19. SEM image of a fracture surfaces of S690Q steel. Sample after a constant load test in seawater. Relative load  $F/F_m = 0.96$ , open circuit potential



Tables 3-5 present critical relative loads, and cathodic current densities at which delayed hydrogen cracking occurs in tested steels. As it can be seen investigated steels and the welded joints have high resistance to hydrogen degradation in hydrogen generating environment.

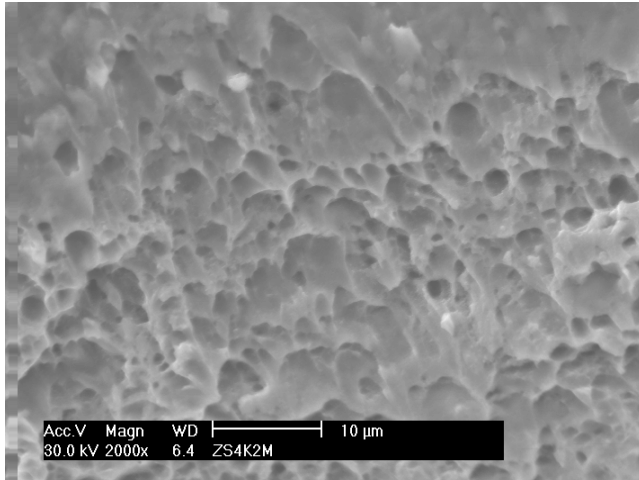


Fig. 20. SEM image of a fracture surfaces of weld metal (SMAW) of S690Q steel. Sample after a constant load test in seawater. Relative load  $F/F_m = 0.96$ , open circuit potential

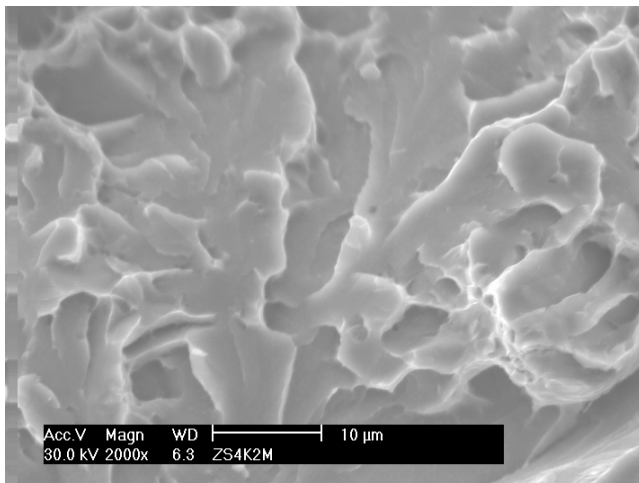


Fig. 21. SEM image of a fracture surfaces of HAZ (SMAW) of S690Q steel. Sample after a constant load test in seawater. Relative load  $F/F_m = 0.96$ , open circuit potential

Steel S690Q tested in seawater both at open circuit potential and cathodic polarisation 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 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 resulting in different mechanical properties (strength, hardness) of steel, and its different susceptibility to hydrogen degradation.

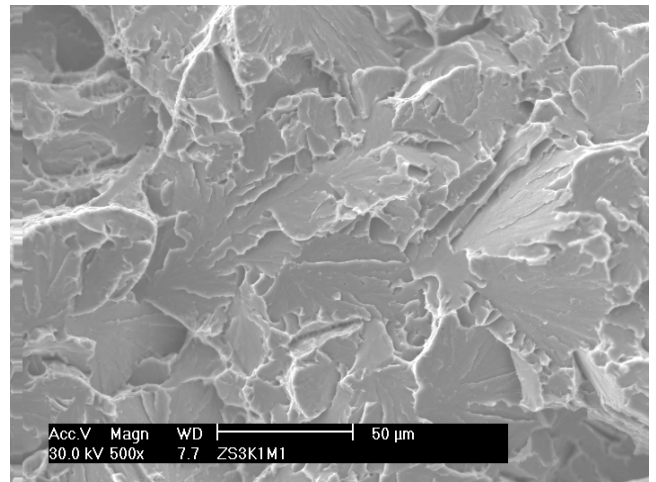


Fig. 22. SEM image of a fracture surfaces of HAZ (SAW) of S690Q steel. Sample after a constant load test in seawater. Relative load  $F/F_m = 0.92$ , cathodic current density  $1 \text{ mA/cm}^2$

Fractographic observations of failed samples revealed various fracture modes according to material and hydrogenation conditions. Base metal samples of S690Q steel revealed quasi-cleavage fracture for test performed at open circuit potential, and under cathodic polarisations (Fig. 19). Samples with SMAW welded joints, tested at open circuit potential, had micro void coalescence (MVC) fracture in the weld metal (Fig. 20), which turned into transgranular cleavage in the heat affected zone (Fig. 21). This observation is consistent with constant load test results where SMAW welded joints had the lower resistance to hydrogen delayed cracking (c.f. Table 5). Welded joints samples tested under cathodic polarisations showed brittle transgranular cleavage and intergranular fracture (Fig. 22).

Obtained results of constant load test and fractographic observations suggest that hydrogen-enhanced localised plasticity (HELP) model is the more applicable mechanism for hydrogen degradation.

Hydrogen delayed cracking occurs at load level as high as flow stress (yield strength) of tested steel and its welded joints. 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.

## 14. Nitride layers as a prevention against hydrogen degradation

Susceptibility of 34CrAlNi7-10 steel and samples with various plasma nitrided layers were evaluated under monotonically increasing load in 0.005 M H<sub>2</sub>SO<sub>4</sub> solution. Slow-strain rate tensile (SSRT) test was carried out under cathodic polarisation. Elongation, reduction in area, fracture energy and tensile strength were chosen as measures of susceptibility to hydrogen embrittlement. Fracture modes of failed samples were examined with the use of scanning electron microscope (SEM) [25-27].

### 14.1. Material and experimental procedure

The structural nitriding steel grade 34CrAlNi7-10 according to PN-EN 10085 was used. The round bar was heat treated at the mill with the following parameters: quenched at 880°C by oil cooling, tempered at 650°C by air cooling, and stress relief annealed at 600°C for 6 hrs. by furnace cooling. The chemical composition of the tested steel is given in Table 6.

Mechanical properties obtained from the tensile test for the steel are presented in Table 7.

Hardness of base metal was measured on a cross section of the steel bar along its diameter using 98.1 N load (10 kG), and hardness of nitrided layers was measured on surface of flat nitrided samples using 4.9 and 9.8 N loads (0.5 and 1 kG respectively), both according to PN-EN 6507-1.

Nitriding was done in the nitrogen-hydrogen (or argon) gas atmospheres with various hydrogen content, i.e. 0%, 30%, and 70%, at the glow discharge at temperature 560°C for 6 hrs. Various contents of hydrogen in atmospheres were chosen to obtain different initial hydrogen concentration in nitrided layer.

The nitrided layers were investigated by X-ray photoelectron spectroscopy (XPS), and Auger electrons spectroscopy (AES) methods with the use of multifunctional PHI 5700/660 electron spectrometer. The analysis was performed on cross sections of nitrided layers. The examinations were conducted in the region extending from the surface down to a depth of 400 µm.

Microstructures of the steel plate and nitrided layers were examined with the use of the optical microscope on cross sections etched with nital.

In order to estimate the degree of hydrogen degradation of tested steel and its modified layers, slow strain rate tensile (SSRT) test was conducted along with PN-EN ISO 7539-7 on round smooth specimens 4 mm in diameter made according to PN-EN ISO 7539-4. The gauge length was 50 mm. Tests were performed

at ambient temperature either in dry air or in 0.005 M H<sub>2</sub>SO<sub>4</sub> solution. The applied strain rate was 10<sup>-6</sup> s<sup>-1</sup>. Tests in acid solution were conducted under cathodic polarisation with constant current density 10 mA/cm<sup>2</sup>. During tests stress-strain curves were recorded on a personal computer. Three samples were used for each parameter.

Fracture surfaces after SSRT test were examined using a scanning electron microscope (SEM) to reveal a mode and mechanism of cracking.

### 14.2. Description of achieved results

The XPS investigations were performed to characterise only the diffusion zone of nitrided layers since examination was performed on a cross section of nitrided samples. Measurement points were placed along the line perpendicular to surface with distances of about 8 µm. A step between measurement points was relatively high comparing to thickness of a compact nitride zone, and hence, thin nitride zone was not analysed.

The whole XPS spectrum of diffusion zone for a nitrided layer on samples 34A2 is presented in Fig. 23. The spectrum exhibits presence of Fe, Cr, Ni, Al, N, O, C, Ca, Na, Cl. Peaks of carbon and oxygen corresponds to absorbate carbon oxides, while peaks of iron and oxygen indicate that surface was covered with iron oxides. Calcium, sodium, and chlorine were from contaminations. Iron, chromium, nickel, and aluminium are components of the steel and nitrides presented in diffusion zone.

The shape of nitrogen N1s line obtained in diffusion zone of nitrided layer of sample 34A2 is given in Fig. 24. The binding energy determined for N1s line corresponds to formation of Fe<sub>4</sub>N.

Distribution of nitrogen and iron concentration in surface layer on sample 34A2 is presented in Fig. 25.

Mean hardness of base metal was 326 HV10. Hardness values for modified layers by nitriding are presented in Table 8.

Microstructure of the steel composed of sorbite. The obtained modified layers consisted of the zone of compact γ' (Fe<sub>4</sub>N) nitride, and the diffusion zone (Figs. 26-28), of the thicknesses given in Table 9.

Elongation, reduction in area, fracture energy and tensile strength obtained from SSRT were chosen as measures of hydrogen degradation (Table 10). Then, relative parameters, determined as the ratio of the appropriate value measured in the air to that measured in acid solution, were calculated (Table 11). It is known from literature that reduction in area is the most sensitive to hydrogen degradation among mechanical properties [4].

Table 6.  
Chemical composition of tested 34CrAlNi7-10 steel

Analysis	Chemical composition, wt %										
	C	Si	Mn	P	S	Cr	Mo	Ni	Al	Cu	
Ladle according to PN-EN 10085:2003	0.30	max	0.40 0,70	max	max	1.50 1.80	0.15 0.25	0.85	0.80 1.20	-	
Control of the bar	0.37	0.40		0.025	0.035			1.15			
	0.37	0.28	0.59	0.008	0.001	1.50	0.25	0.95	0.90	0.07	

Table 7.  
Mechanical properties (longitudinal direction) of the bar made of 34CrAlNi7-10 steel

Samples	Yield Strength MPa	Tensile Strength MPa	Elongation %	Reduction in Area %
Base metal	842	988	19.0	59

Table 8.  
Vickers hardness test results of modified nitrided layers

Codes of specimens	Vickers hardness	
	HV0.5	HV1
34A1	960	960
34A2	1080	1090
34A3	1080	1080

Table 9.  
Parameters of the surface treatment and the thickness of the modified layers

Codes of samples	Parameters of nitriding	Thickness of compact nitrides zone, $\mu\text{m}$	Thickness of diffusion zone, $\mu\text{m}$
34R	base metal - as received	-	-
34A1	70%N <sub>2</sub> + 30%Ar	12	200-225
34A2	70%N <sub>2</sub> + 30% H <sub>2</sub>	6	200-225
34A3	30%N <sub>2</sub> + 70% H <sub>2</sub>	10	200-225

Table 10.  
Mean values of hydrogen degradation parameters of 34CrAlNi7-10 steel and samples with various nitrided layers

Sample	Elongation %	Reduction in area, %	Fracture energy MJ/m <sup>3</sup>	Tensile strength MPa
34A1-K	2.2	3.1	12	890
34A1-P	6.5	8.3	51	949
34A2-K	2.3	3.5	13	874
34A2-P	6.6	8.3	53	959
34A3-K	2.0	3.5	10	851
34A3-P	7.3	12.9	59	993
34R-K	8.9	12.6	72	969
34R-P	12.4	62.7	103	972

A1, A2, A3 – various surface treatments; P – tests performed in the air; K – tests performed in acid solution

Table 11.  
Relative values of plasticity hydrogen degradation parameters of 34CrAlNi7-10 steel and samples with various nitrided layers

Sample	Elongation %	Reduction in area, %	Fracture energy %	Tensile strength %
34A1	33.8	37.3	23.5	93.8
34A2	34.8	42.2	24.5	91.1
34A3	27.4	27.1	16.9	85.7
34R	71.8	20.1	70.0	99.6

A1, A2, A3 – various surface treatments; 34R – base metal without nitrided layer

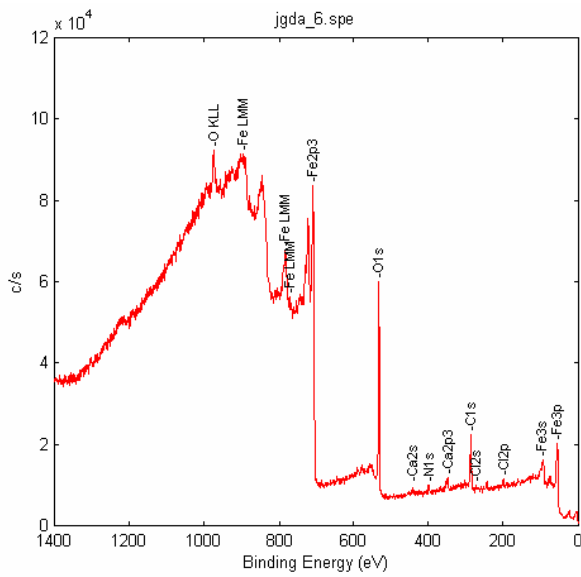


Fig. 23. The whole XPS spectrum for diffusion zone of nitrated layer on sample 34A2

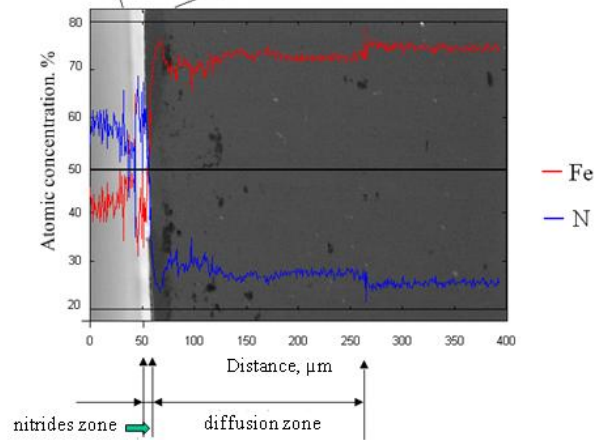
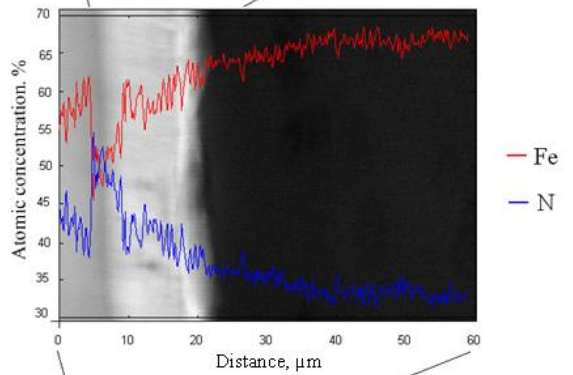
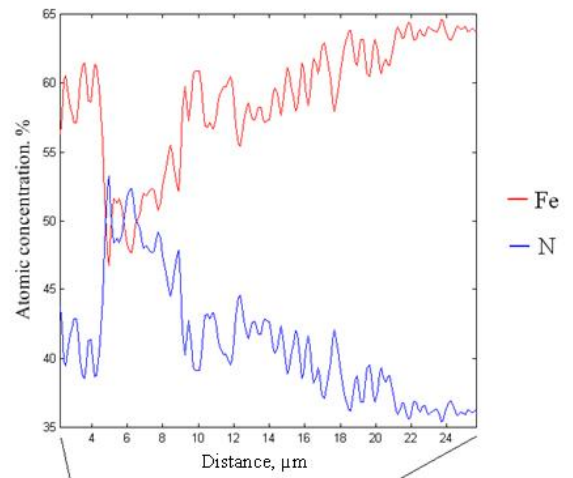


Fig. 25. AES line profiles of chemical composition (nitrogen and iron) with SEM view of nitrated layer on sample 34A2

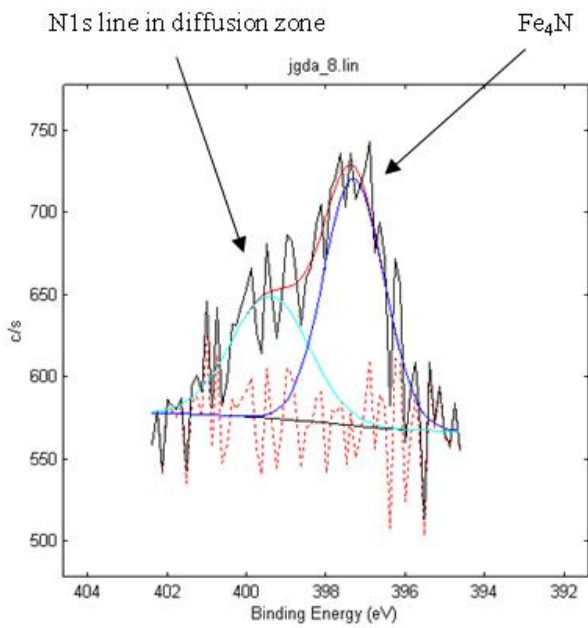


Fig. 24. The shape of nitrogen N1s line (XPS) in diffusion zone of nitrated layer on sample 34A2



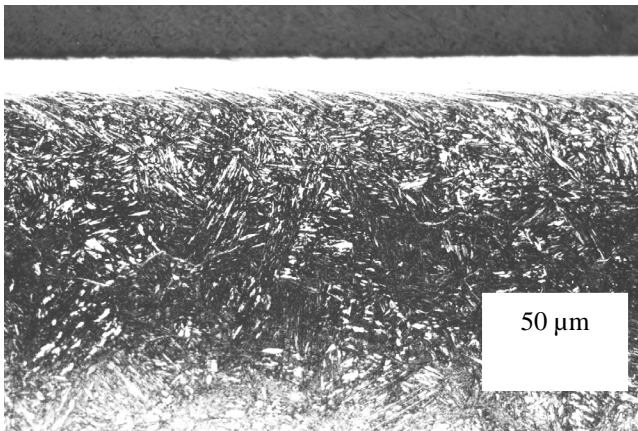


Fig. 26. Microstructure of plasma nitrided layer. Sample 34A1. Compact nitride and diffusion zones. Nital etching



Fig. 27. Microstructure of plasma nitrided layer. Sample 34A2. Compact nitride and diffusion zones. Nital etching

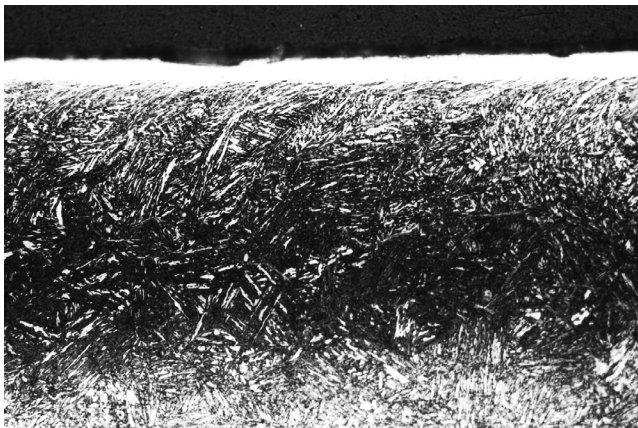


Fig. 28. Microstructure of plasma nitrided layer. Sample 34A3. Compact nitride and diffusion zones. Nital etching

All tested samples revealed susceptibility to hydrogen degradation under hydrogenation. Samples with nitrided layer have lower lost of relative reduction in area than base metal samples. In the case of elongation the base metal has lower lost of plasticity. The nitrided layer established in standard atmosphere 30% H<sub>2</sub> and 70% N<sub>2</sub> has the highest resistance to hydrogen degradation evaluated in SSRT test.

Plasma nitriding strongly decreases the absorption of hydrogen by impeding both its entry and transport in the modified layer for pure iron, low and medium carbon steels, and low-alloy steels. The effect of nitrogen is attributed to a lower solubility of hydrogen in the implanted layer, and its slower transport due to trapping at nitride precipitates. The compound zone controls the penetration of hydrogen mainly by affecting its entry. The impediment of hydrogen transport results from the lower hydrogen diffusivities in the diffusion zone.

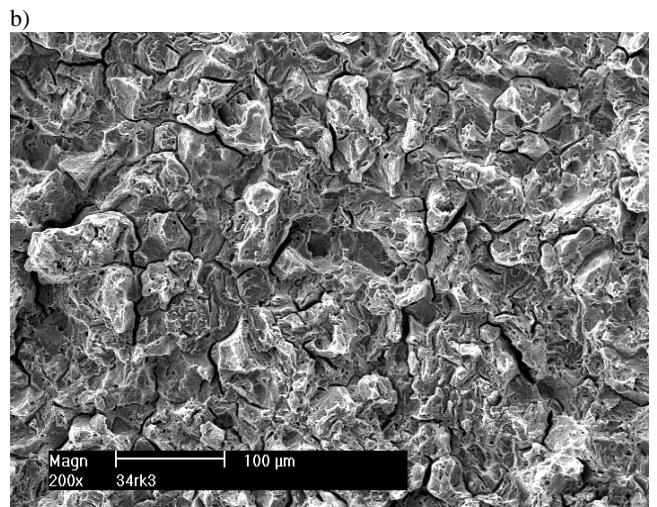
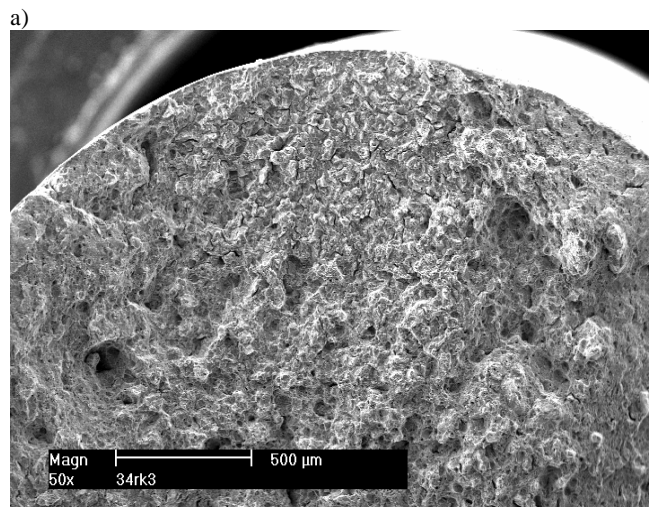


Fig. 29. SEM images of fracture surface of 34R sample after SSRT tested in acid solution under cathodic polarisation. Magnification: a) 50x, b) 200x



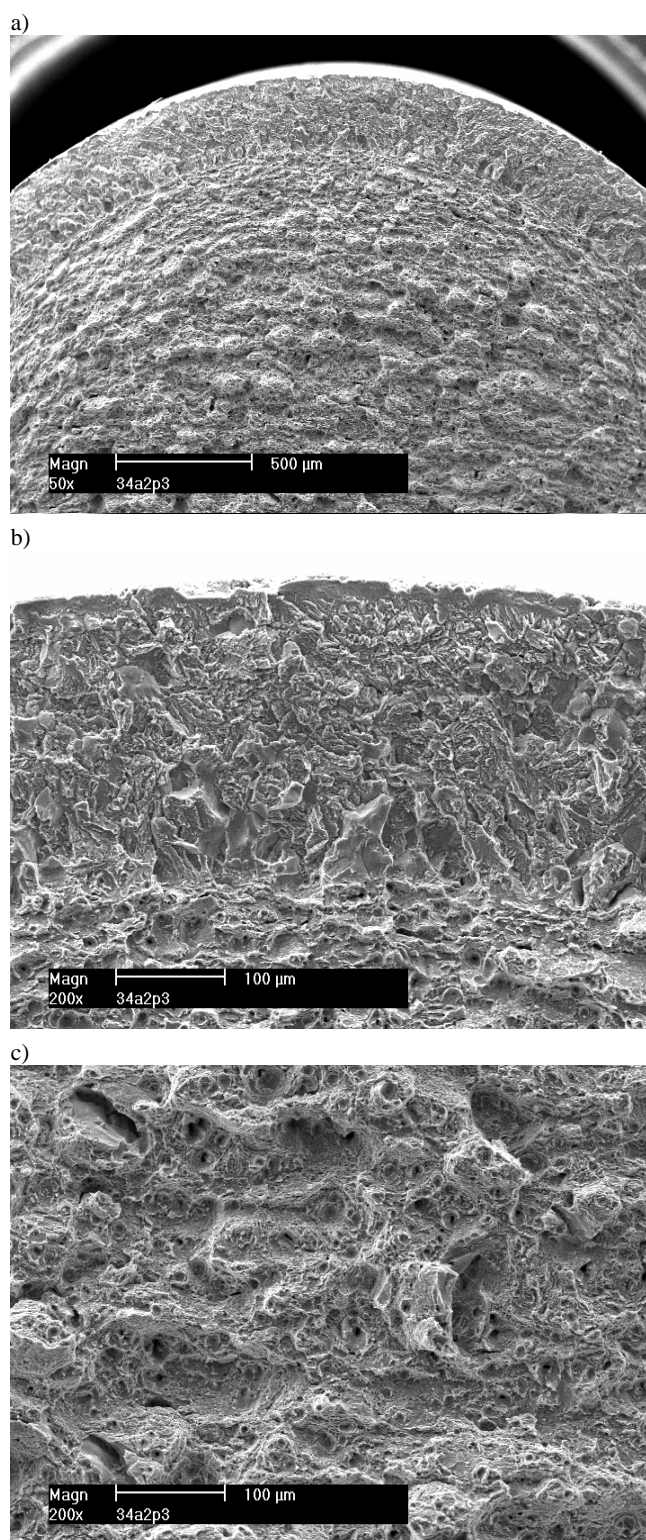


Fig. 30. SEM images of fracture surface of 34A2 sample after SSRT tested in the air. a) macroscopic view, b) modified layer, c) core of base metal

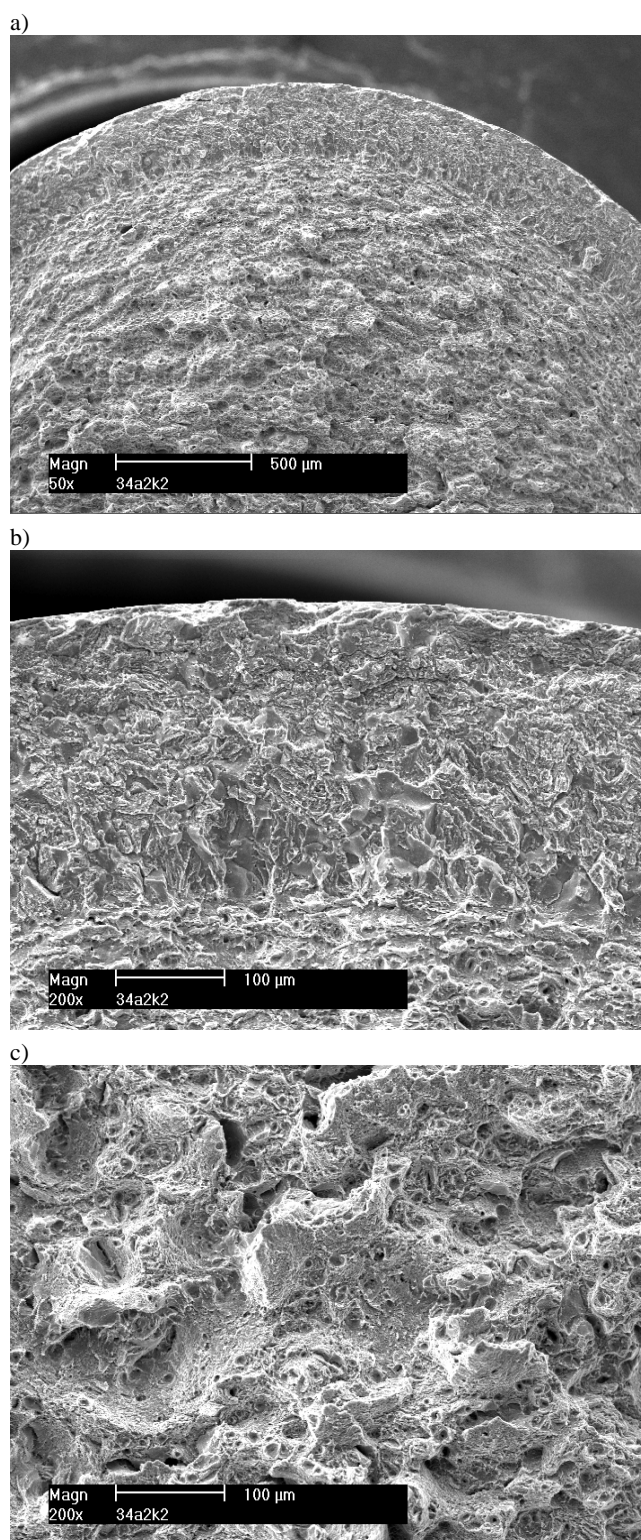


Fig. 31. SEM images of fracture surface of 34A2 sample after SSRT tested in acid solution under cathodic polarisation. a) macroscopic view, b) modified layer, c) core of base metal



The diffusion coefficient of hydrogen in the compound zone is much lower than in the diffusion zone, but the compound zone is not decisive in hindrance of hydrogen transport since this zone is relatively thin. The diffusion zone impedes the hydrogen transport much stronger [28].

Under the increasing load and hydrogen generating environments plasma nitrided layers are effective barriers to hydrogen entry into a bulk of steel, which was confirmed by the electrochemical permeation Devanathan-Stachursky test [26].

Samples with nitrided layers and absorbed external hydrogen revealed no increase of hydrogen embrittlement comparing to the same samples without dissolved hydrogen. Evidences of likely increased plasticity of nitrided layers with absorbed hydrogen were observed. These evidences are the following:

- values of reduction in the area at the same level,
- fractographic observations i.e. lower percentage of cleavage fracture area.

Fractographic observations of failed base metal samples tested in acid solution under cathodic polarisation revealed intergranular and cleavage transgranular fracture mode (Fig 29). Fracture composed of ductile and quasi-cleavage mode in the core of nitrided samples tested both in the air and acid solution under cathodic polarisation (Fig. 30-31) is an evidence of protective action of nitrided layers against hydrogen diffusion into a bulk of steel.

## 15. Conclusions

- Tested high-strength S690Q 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 than for the base metal.
- Tested S690Q steel and its welded joints could be safely utilized in marine constructions under cathodic protection provided that overprotection does not take place.
- Hydrogen-enhanced localized plasticity (HELP) model is more applicable mechanism of hydrogen degradation than others for high-strength welded joints in seawater environment.
- High-strength S690Q steel and its welded joints have high resistance to hydrogen delayed cracking in seawater environment.
- Under the critical load and cathodic current density notched samples of S690Q steel prematurely failed and hydrogen-enhanced localised plasticity (HELP) model is a viable degradation mechanism.
- Under the increasing load and hydrogen generating environments plasma nitrided layers are effective barriers to hydrogen entry into structural steel,
- Evidences of likely increased plasticity of nitrided layers with absorbed hydrogen were observed.
- Plasma nitriding may prevent hydrogen charging of machines and vehicles parts in hydrogen generating environments, and thus, decreasing susceptibility to hydrogen embrittlement.

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## References

- [1] S.P. Lynch, Failures of structures and components by environmentally assisted cracking, *Engineering Failure Analysis*, 2 (1994) 77-90.
- [2] P.F. Timmins, *Solutions to hydrogen attack in steels*, AMS International, 1997.
- [3] *ASM Handbook. Vol. 11 Failure Analysis and Prevention*. ASM International, 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] L. Coudreuse, C. Renaudin, P. Bocquet, L. Cadiou, Evaluation of hydrogen assisted cracking resistance of high strength jack-up steels, *Marine Structures* 10 (1997) 85-106.
- [6] J.V. Sharp, J. Billingham, M.J. Robinson, The risk management of high-strength steels in jack-ups in seawater, *Marine Structures* 14 (2001) 537-551.
- [7] Offshore Technology Report – OTO 1999 056, A review of the effects of microstructure on the hydrogen embrittlement of high strength offshore steels, Health and Safety Executive, 1999.
- [8] J. Cwiek, High strength weldable steels, *Mechanical Review* 9 (1996) 9-15 (in Polish).
- [9] H.K. Birnbaum, I.M. Robertson, P. Sofronis, D. Teter, Mechanisms of hydrogen related fracture. A review, *Proceedings of the 2<sup>nd</sup> International Conference “Corrosion Deformation Interaction”*, The Institute of Materials, London, 1997, 172-195.
- [10] T.J. Carter, L.A. Cornish, Hydrogen in metals, *Engineering Failure Analysis* 8 (2001) 113-121.
- [11] J.P. Hirth, Effects of hydrogen on the properties of iron and steel, *Metallurgical Transactions A* 11 (1980) 861-890.
- [12] A. Zieliński, Hydrogen degradation of nonferrous metals and alloys, Gdańsk Scientific Society, Gdańsk, 1999 (in Polish).
- [13] J. Woodtli, R. Kieselbach, Damage due to hydrogen embrittlement and stress corrosion cracking, *Engineering Failure Analysis* 7 (2000) 427-450.
- [14] S. Serebrinsky, E.A. Carter, M. Ortiz, A quantum-mechanically informed continuum model of hydrogen embrittlement, *Journal of Mechanics and Physics of Solids* 52 (2004) 2403-2430.
- [15] T.P. Pernga, J.K. Wub, A brief review note on mechanisms of hydrogen entry into metals, *Materials Letters* 57 (2003) 3437-3438.
- [16] M.V. Biezma, The role of hydrogen in microbiologically influenced corrosion and stress corrosion cracking, *International Journal of Hydrogen Energy* 26 (2001) 515-520.
- [17] R.A. Oriani, J.P. Hirth, M. Smialowski (eds.) *Hydrogen degradation of ferrous alloys*, Noyes Publ. Park, Ridge, USA, 1985.
- [18] M. Walsh, T. Ford, R. Mitchell, Influence of hydrogen-producing bacteria on hydrogen uptake by steel, *Corrosion* 45/9 (1989) 705-709.
- [19] S.P. Lynch, A commentary on mechanisms of environmentally assisted cracking, *Proceedings of the 2<sup>nd</sup> International Conference „Corrosion-Deformation Interactions”* CDI’96, Nice, 1996, 206-219.

- [20] P. Sofronis, Y. Liang, N. Aravas, Hydrogen induced shear localization of the plastic flow in metals and alloys, *European Journal of Mechanics - A/Solids* 20 (2001) 857-872.
- [21] Th. Magnin, *Advances in Corrosion-Deformation Interactions*, Trans Tech Publications, 1996.
- [22] J. Ćwiek, Hydrogen degradation of high strength weldable steels, *Journal of Achievements in Materials and Manufacturing Engineering* 20 (2007) 223-226.
- [23] 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.
- [24] B. Świczko-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.
- [25] A. Zieliński, J. Ćwiek, M. Błaszkiwicz, Effect of plasma nitrated layers on low-alloy steel on its hydrogen degradation, *Journal of Achievements in Materials and Manufacturing Engineering* 17 (2006) 213-216.
- [26] S. Sobieszczyk, E. Łunarska, J. Ćwiek, A. Zieliński, K. Nikiforow, Hydrogen charging of plasma nitrated steel in acid solution, *Journal of Achievements in Materials and Manufacturing Engineering* 17 (2006) 205-208.
- [27] J. Ćwiek, Plasma nitriding as a prevention method against hydrogen degradation of steel, *Journal of Achievements in Materials and Manufacturing Engineering* 36/1 (2009) 25-32.
- [28] T. Zakroczyński, N. Łukomski, J. Flis, The effect of plasma nitriding-base treatments on the absorption of hydrogen by iron, *Corrosion Science* 37 (1995) 811-822.
- [29] 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.
- [30] PN-EN 10002-1:2004 Metallic materials – Tensile testing – Part 1 – Method of test at ambient temperature.
- [31] PN-EN 1321:2000 Destructive tests on welds in metallic materials – Macroscopic and microscopic examination of welds.
- [32] PN-EN ISO 6507-1: 1999. Metallic materials. Vickers hardness test – Part 1: Test method.
- [33] PN-EN ISO 7539-4:2000 Corrosion of metals and alloys – Stress corrosion testing – Part 4: Preparation and use of uniaxially loaded tensions specimens.
- [34] PN-EN ISO 7539-7:2000 Corrosion of metals and alloys – Stress corrosion testing – Part 7: Slow strain rate testing.
- [35] PN-EN 2832:2001 Aerospace series – Hydrogen embrittlement of steels – Notched specimen test.
- [36] PN-66/C-06502. Substitute seawater
- [37] PN-EN 10085:2003 Nitriding steels – Technical delivery conditions.