

## Prevention methods against hydrogen degradation of steel

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### Properties

#### ABSTRACT

**Purpose:** of this paper is presentation of mechanisms and forms of hydrogen degradation in steel along with pointing out methods for hydrogen degradation prevention.

**Design/methodology/approach:** Hydrogen degradation of steel is a form of environmentally assisted failure which is caused by the action of hydrogen often in combination with residual or applied stress resulting in reduction of plasticity, load bearing capacity of a component, and cracking.

**Findings:** The sources of hydrogen in steel were presented. Forms of hydrogen presence in metals, mechanisms of hydrogen degradation, and types of hydrogen induced damage were discussed in details. Five specific types of hydrogen induced damage to metals and alloys could be distinguished: hydrogen embrittlement, hydrogen-induced blistering, cracking from precipitation of internal hydrogen, hydrogen attack, cracking from hydride formation.

**Practical implications:** Methods for hydrogen degradation prevention include: selection of suitable material, modifying environment to reduce hydrogen charging, and use of surface coatings and effective inhibitors.

**Originality/value:** Originality the paper outlines the problem of hydrogen degradation of steel and other alloys, delivering knowledge to undertake preventive or remedial actions in order to avoid hydrogen induced degradation.

**Keywords:** Crack resistance; Metallic alloys; Hydrogen; Hydrogen degradation

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### 1. Introduction

Synergic action of stress and environment may result in various types of degradation of metallic materials. 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 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 charging rate [3].

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 constructions made with such steels have been used in service without serious problems in various environments. Steels having a tensile strength greater than 1000 MPa are susceptible to hydrogen embrittlement, and steels with tensile strength over 1200 MPa are especially susceptible and may fail at stress much below their yield strength [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 constructions, long distance sour gas transportation pipeline, car and aircraft components [1, 2].

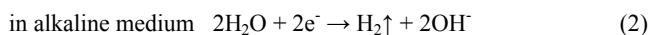
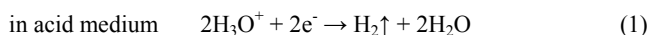
Hydrogen embrittlement has been the cause of failures in high-strength structural steels used in the offshore industry. The problem is due to absorption of hydrogen from seawater, which is promoted when cathodic protection is applied to the steel to control corrosion. Hydrogen induced cracking is still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

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

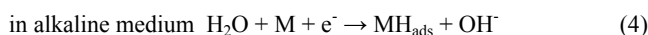
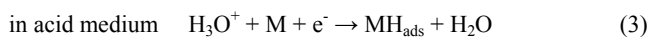
## 2. Sources of hydrogen in steel

The sources of hydrogen in steel are many: gaseous hydrogen, liberation of atomic hydrogen by the iron-water or iron-H<sub>2</sub>S reactions, decomposition of water molecules, electrolytic and corrosion processes including a cathodic reaction.

During pickling in mineral acids, cathodic electrochemical 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 a 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<sub>2</sub>, 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<sub>ads</sub>) 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<sub>abs</sub>):



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 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 [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 sulfate-reducing bacteria in sea-water [18].

Sulfate Reducing Bacteria or “desulfovibrio” bacteria (SRB), a heterogeneous group of anaerobic heterotrophic bacteria, which use inorganic sulfate as a final electron acceptor in respiration, are the main bacteria responsible for the numerous microbiologically influenced corrosion (MIC) cases. Hydrogen sulfide as a result of the anaerobic activity of SRB reacts with iron and creates H<sub>2</sub>:



Additionally, enlarged hydrogen absorption, with SRB presence, is due to promoting action of H<sub>2</sub>S near material surface [17].

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. 1). 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 cannot 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 pick-up during fusion welding operations is a mechanism in which hydrogen, dissociated from water present as a 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 surfaces is absorbed into the molten weld pool and remains trapped on solidification.

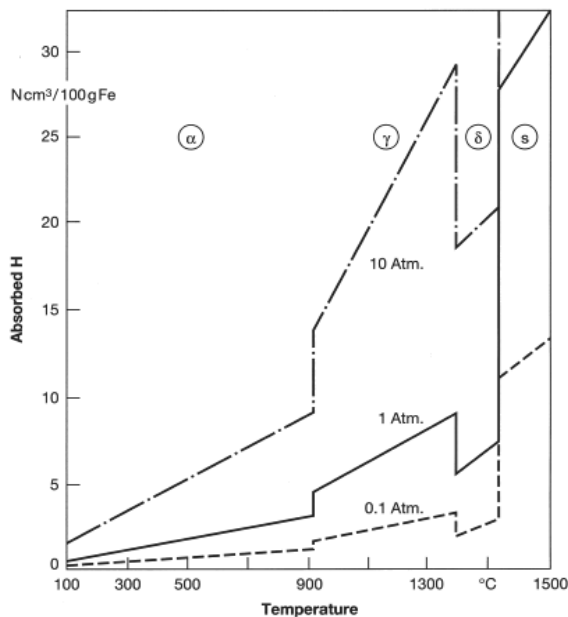


Fig. 1. Solubility of hydrogen in iron as a function of temperature and pressure [2, 13]

### 3. Forms of hydrogen presence in metals

Hydrogen dissolves in metals as an atom or screened proton rather than as a hydrogen molecule. 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,  $H_2$ . 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 absorption of hydrogen from a gas phase requires the presence of atomic (nascent) hydrogen on the metal surface. The formation of atomic hydrogen on a metal surface exposed to a gaseous hydrogen environment requires the disassociation of hydrogen molecules. The amount of hydrogen absorbed will depend on the efficiency of the dissociation process which, in turn, depends on the condition of the metal surface. Thin oxide films on metal surfaces significantly reduce the ability of hydrogen to dissociate thus the presence of an oxide has the same impact on hydrogen absorption as lowering the hydrogen pressure would have.

Exposure of steels to acidic solutions generally charges more hydrogen into the metal than exposure to hydrogen gas unless the gas pressure is very high. The difference between gaseous charging and chemical charging of hydrogen is due to differences in the concentration of nascent hydrogen atoms at the metal surface. During gaseous charging, nascent hydrogen atoms are

formed by dissociation of hydrogen molecules while during chemical charging nascent hydrogen is formed as the result of cathodic reactions. The concentration of nascent hydrogen atoms on the surface of a metal during acid pickling may be orders of magnitude higher than the nascent hydrogen atom concentration created by exposure to hydrogen gas.

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. The tendency for acid exposures to charge hydrogen into a metal is one reason the acid based cleaning solutions should be used with caution or not to be used at all. 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:



Most of the hydrogen atoms thus formed quickly combine 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.

The absorbed hydrogen in a metal can be present in either of two locations in the microstructure:

- interstitial sites in the lattice,
- sites typically associated with crystalline defects.

Hydrogen absorption causes the iron lattice to expand because the effective size of the atomic hydrogen is larger than the size of the interstitial site (a void in crystalline lattice). This size difference causes hydrogen to prefer extraordinary sites where a void is expanded and the atomic hydrogen is more readily accommodated. Examples of extraordinary sites include grain boundaries, vacancies, dislocations.

The cold work process increased the dislocation density and vacancy concentrations in steel, and thus the amount of absorbed hydrogen also increased. The concentration of hydrogen at the extraordinary sites in ferritic or martensitic steels can greatly exceed the concentration of hydrogen at the normal interstitial sites. Usually, the hydrogen at extraordinary sites is termed as "trapped hydrogen" and the hydrogen at the normal interstitial sites is termed as "dissolved or diffusable hydrogen".

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 since lattice defects (present areas where the lattice strain induced by the solute hydrogen atom is reduced) 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 temperature above 200°C, known as “high temperature hydrogen attack” [2].

#### 4. Mechanisms of hydrogen degradation of metals

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, 9, 11, 19-21].

##### *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 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 (Fig. 3). Mechanism proposed by Lynch.

##### *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 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 localized deformation that leads to highly localized failure by ductile processes, while the macroscopic deformation remains small.

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 an 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 could 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 centers results in enhanced dislocation mobility. This phenomenon is supported by strong experimental evidence and has been 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 relative to the flow stress in the homogeneously deforming volume, but the mechanism by which hydrogen causes shear localization has not been established as of 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. 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.

## **5. Types of hydrogen induced damage**

Hydrogen degradation is a form of environmentally assisted failure which is caused by the action of hydrogen often in combination with residual or applied stress resulting in reduction of plasticity, load bearing capacity of a component, and cracking. Many metals and alloys, like Fe, Ni, Al, Ti, Zr, Ta, Hf, Nb, V, W, Mo and U are susceptible to hydrogen degradation. It could be stated that almost all engineering materials are not immune to harmful hydrogen influence.

Hydrogen degradation manifests in various modes of material degradation and failure each of which is highly specific to the alloy-environment system. Hydrogen reduces the service life of many metallic components and structures. Such reductions may be manifested as blisters, as a decrease in fatigue resistance, as enhanced creep or stress corrosion cracking, as the precipitation of a hydride phase and, most commonly, as unexpected brittle failure.

Five specific types of hydrogen induced damage to metals and alloys could be distinguished:

- hydrogen embrittlement,
- hydrogen-induced blistering
- cracking from precipitation of internal hydrogen,
- hydrogen attack,
- cracking from hydride formation.

Except for hydrogen embrittlement, a phase transformation is present in each of the above mentioned hydrogen damage process. Types of hydrogen damage that involve phase transformations are relatively easy to understand may be minimized by paying attention to the damage causing process. Understanding the damage process involved in hydrogen embrittlement is more elusive and avoiding the damage processes has proven difficult [22-25].

#### *Hydrogen Induced Blistering*

Hydrogen induced blistering occurs during or after hydrogen has been absorbed by the metal. The mobile hydrogen atoms collect at traps in the alloy. Hydrogen traps include the interface between inclusions and the metallic matrix as well as laminations in a wrought structure. Such interfaces are mechanical bonds and

provide surfaces inside the metal. As hydrogen collects at this surface the nascent atoms recombine to molecular form and pressure at the lamination or the inclusion-matrix interface occurs. The magnitude of this pressure will depend on the concentration of absorbed hydrogen in the metal, the trapped-to-dissolved hydrogen ratio, and the temperature.

Blister formation requires that an alloy [25]:

- contains inclusions or other internal surfaces where hydrogen can accumulate,
- absorb sufficient hydrogen to pressurize the internal surfaces where the accumulation occurred,
- remain ductile after hydrogen absorption.

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.

#### *Cracking from Precipitation of Internal Hydrogen*

Cracks that result from the precipitation of internal hydrogen have been termed fisheyes shatter cracks, and flakes. These forms of hydrogen damage occur in forgings, welds and castings and are attributed to hydrogen absorption in the molten metal. Sources of hydrogen include the formation of nascent hydrogen by the reaction between metal and moisture in the environment. This source of hydrogen and the potential for subsequent hydrogen induced damage to welds is one reason that welding rods are frequently dried by storing and/or heating in a low temperature furnace.

The solubility of hydrogen decreases significantly during solidification and the excess hydrogen precipitates at voids, pores and other internal surfaces. As the pressure in the region of hydrogen precipitation increases the stresses at the tip of the void increase. The presence of high pressure hydrogen at the surface of many metals and alloys causes surface defects to extend in a macroscopically brittle mode.

Fisheyes reduce the cross section of the metal, provide significant stress concentrations and may act as initiation sites for fatigue. Shielding the molten metal from moisture is a key to preventing fisheye formation. This can be accomplished by controlling slag chemistry, vacuum melting and/or the use of dry environments. Even if hydrogen is present in the metal, fisheye formation may be prevented by heating the metal to temperatures slightly above room temperature and giving the hydrogen time to egress from the metal.

The differences between flakes and fisheyes are that flakes form during processing while fisheyes form during testing or service. And in the case of fisheyes hydrogen gas precipitates along nonmetallic inclusion-metal interfaces, so an inclusion is observed in the centre of fisheyes brittle fracture region.

#### *Hydrogen Attack*

Hydrogen attack occurs when absorbed hydrogen interacts with alloying or impurity elements in the microstructure to form an insoluble, generally gaseous, phase. Two important examples of such attack are hydrogen interactions with copper oxide inclusions in copper alloys to produce steam and hydrogen interactions with carbides in steel to produce methane. These are

elevated temperature processes termed as “high temperature hydrogen attack”, and that generally lead to the formation of pressurized, grain boundary cavities.

Hydrogen can reduce copper oxide, producing copper and water through the reaction:



The exposure of steel components to high temperatures and high hydrogen pressures can alter the microstructure, degrade the strength and ultimately cause fracture. The exposure also causes hydrogen to be absorbed by the steel. The absorbed hydrogen is very mobile and begins to accumulate at pores and micropores associated with the grain boundary inclusions or other microstructural defects. Inside the pores the absorbed nascent hydrogen recombines to form hydrogen molecules which react with carbon to form methane. This reaction coupled with the cementite decomposition reaction (the same reaction that causes surface decarburization) thermodynamically favors methane formation when the temperature exceeds approximately 200°C.



The reactions occur at grain boundaries, where the methane gas exerts internal pressure and forms fissures or elongated pores in a metal. This phenomenon has been 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.

The behavior of the common engineering steels in a hydrogen environment has been summarized 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]. The Nelson Curves are published by the American Petroleum Institute (API), and these curves delineate the safe operating ranges, in terms of temperature and hydrogen partial pressure, for various alloys used in the petrochemical industry. The curves are primarily based on practical experience and engineering judgment. Analysis of the curves demonstrates that the maximum hydrogen pressure specific steels can withstand without hydrogen attack decreases as the temperature increases and that hydrogen attack does not occur below a certain, alloy dependent temperature.

#### *Cracking from Hydride Formation*

Zirconium, titanium, tantalum and other transition, rare earth metals form hydrides when the hydrogen concentration exceeds a certain level. When the hydrogen content of zirconium, titanium, uranium and other hydride forming metals exceeds the solubility limit, metal hydrides precipitate. The hydrides are typically low density, brittle compounds whose presence degrades the ductility of the alloy. Both  $\alpha$  (ferrite) and  $\gamma$  (austenite) phases of iron form only solid solutions with hydrogen and no evidence of hydride has been observed.

#### *Hydrogen Embrittlement*

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].

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.

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). Delayed cracking at stress below the yield strength is termed as hydrogen stress cracking (HSC).

Brittle failure by cracking under the combined action of tensile stress and corrosion in the presence of water and hydrogen sulfide is called sulfide 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 (below 1000 h). Therefore, tension, notched, and precracked specimens and fracture methods are widely utilized in the evaluation for HEC.

The susceptibility of steel to hydrogen embrittlement during a tensile test is dependent on the test temperature and strain rate, and hydrogen embrittlement could occur when the applied stress level is below the yield strength of the material. In this case the hydrogen embrittlement process is called as delayed failure/cracking.

The susceptibility of a material to hydrogen embrittlement is temperature dependent primarily for two reasons:

- the tendency for hydrogen segregation to regions of lattice dilation decreases as the temperature increases,
- the mobility of hydrogen decreases as the temperature decreases.

These two effects combine to maximize embrittlement susceptibility at an intermediate temperature. The temperature of maximum embrittlement susceptibility varies with alloy and metallurgical condition, although this maximum is often near room temperature.

## 6. Prevention or remedial action

In order to produce preventative measures, both the source of the hydrogen and the degradation mechanisms 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 degradation forms are as follows:

1. internal cracking or blistering
  - use of steel with low levels of impurities (i.e. sulfur 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. hydrogen attack at high temperature
  - 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).

Minimizing hydrogen content in steel could be obtained by good steel making practice e.g. vacuum melting and degassing techniques. Moist raw materials should not be used and enough time should be given for solidification of the molten metal so as to liberate hydrogen trapped due to decreasing solubility.

Blistering prevention include:

- cleanliness of alloys to preclude the presence of large internal surfaces. Shape of inclusions greatly influences the susceptibility. Elongated inclusions are dangerous and spherical shape is desirable. Such shapes can be achieved by rare earth addition during secondary refining of steel.
- use of cleaning and processing technologies that minimize hydrogen absorption,
- post process heating to cause hydrogen egress from the metal,
- use of inhibitors to minimize corrosion reactions,
- selection of alloys that show low tendency for hydrogen segregation at extraordinary sites (for example austenitic steels rather than ferritic or martensitic steels).

The approach to minimize HIC is to impede hydrogen entry into steel. This can be achieved by direct deposition of a solid on the surface so that hydrogen entry is lowered. In some cases corrosion products formed on the surface also act as barrier to hydrogen entry. Coating steel with Cd, Au, Ag, Pt, Cu, Al, austenitic steel or nitrides and oxides surface layers will lower hydrogen diffusion inside steel. Providing hydrogen with surface traps is another alternative. Ion implantation of Ti has reduced hydrogen entry by providing atomic traps at the surface. Similarly amorphous layers obtained by implanting phosphorus ion on steel has reduced the hydrogen permeation rate through composite material.

Elements such as As, Se, Te, S, P, Sn, Hg, Pb and Bi that promote hydrogen entry by inhibiting hydrogen recombination reaction should be strictly avoided in hydrogen ion-containing environments. These elements when present inside steel segregate to grain boundaries and should be avoided as much as possible.

To avoid HIC, HEC, HSC during welding, the amount of hydrogen entering the weld metal can be limited by the use of clean, low hydrogen consumables. Electrodes should be stored at an appropriate temperature in ovens or used from freshly opened airtight containers. Cleanliness of weld preparation, welding wire and welding apparatus is also important. Paint, rust, grease, degassing agents can all be hydrogen sources. An additional approach to hydrogen control is to allow hydrogen removal by diffusion so that the levels are reduced to acceptable values by the time the weld has cooled. This is done by preheating which decreases the cooling rate and allows more time for the hydrogen to diffuse. Moisture and contamination are also burned off by this. Using higher welding heat inputs also increases the weld thermal cycle time.

In steels with electrolytic coatings (zinc, cadmium) 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).

## 7. Conclusions

- Hydrogen degradation of steel is a form of environmentally assisted failure which is caused by the action of hydrogen often in combination with residual or applied stress resulting in reduction of plasticity, load bearing capacity of a component, and cracking,
- Five specific types of hydrogen induced damage to metals and alloys could be distinguished: hydrogen embrittlement, hydrogen-induced blistering, cracking from precipitation of internal hydrogen, hydrogen attack, cracking from hydride formation.
- Methods for hydrogen degradation prevention include: selection of suitable material, modifying environment to reduce hydrogen charging, and use of surface coatings and effective inhibitors.

## 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 Int., 1997.
- [3] ASM Handbook. Vol. 11 Failure Analysis and Prevention. ASM Int., 1986.
- [4] N. Eliaz, A. Shachar, B. Tal, D. Eliezer, Characteristic of hydrogen embrittlement, stress corrosion cracking and tempered martensite embrittlement in high-strength steels, *Engineering Failure Analysis* 9 (2002) 176-184.
- [5] 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. Ćwiek, 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, 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*, 11A (1980) 861-890.
- [12] A. Zieliński, Hydrogen degradation of nonferrous metals and alloys, Gdansk Scientific Society, Gdansk, 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 and M. Smialowski (eds.) Hydrogen degradation of ferrous alloys, Noyes Publ. Park, Ridge, USA, 1985.
- [18] M. Walsh, T. Ford, and 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 Second International Conference on „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, Hydrogen degradation of high strength steels, *Journal of Achievements in Materials and Manufacturing Engineering* 37/2 (2009) 193-212.
- [24] J. Ćwiek, Plasma nitriding as a prevention method against hydrogen degradation of steels, *Journal of Achievements in Materials and Manufacturing Engineering* 36/1 (2009) 25-32.
- [25] M.R. Louthan, Jr., Hydrogen Embrittlement of Metals: A Primer for the Failure Analyst, US Department of Energy Document WSRC-STI-2008-00062.