## Appendix I –

# Theory of Hydrogen Embrittlement and Stress Corrosion Cracking

by

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## 1. Mechanisms of Hydrogen Embrittlement

This purpose of this appendix is to review the fundamental characteristics of hydrogen embrittlement and stress corrosion cracking of high-strength steels, particularly in relation to galvanized ASTM A354 Grade BD rods.

In general, hydrogen can degrade the mechanical behavior of steel in several ways. For mild steel, dissolved hydrogen can produce loss of ductility at low concentrations, and blistering due to internal pressure of molecular hydrogen at high concentrations. At high temperatures, hydrogen can react with the carbon in steel to form methane, with significant loss of mechanical properties. In the case of high-strength steel, small amounts (0.001-0.1 ppm) of dissolved hydrogen can cause slow crack growth under sustained tensile loads leading to brittle fracture.

When high-strength steels are subjected to sustained tensile loads under normal ambient conditions, dissolved hydrogen is attracted to regions of high tensile stress. As it diffuses to high-stress regions, it is adsorbed on planes of weakness, such as grain boundaries and cleavage planes, where it reduces the attractive forces between iron atoms. When the force required for decohesion of these planes is reduced to less than that required to cause plastic flow, slow crack growth occurs.

As first described by Petch and Stables [1], and Petch [2], decohesion occurs because of a reduction in surface energy due to the adsorption of hydrogen on the planes of greatest weakness. As discussed by Oriani [3] and McMahon [4], decohesion occurs atom-by-atom as hydrogen atoms diffuse to the planar surfaces.

It is now widely accepted that stress corrosion cracking of high-strength, quenchedand-tempered steel exposed to aqueous environments occurs by a hydrogen embrittlement mechanism. Others have reviewed the theory, testing, and phenomenology of stress corrosion cracking and hydrogen embrittlement in highstrength metals in detail [3-8].

Four essential factors are simultaneously required to produce hydrogen embrittlement of high-strength steel:

- Source of hydrogen
- Susceptible steel
- Sustained or slowly increasing tensile load
- Load that exceeds a critical threshold value.

#### 2. Sources of Hydrogen -- Internal vs. Environmental

**Internal Hydrogen** -- There are numerous ways that hydrogen can enter steel during processing. These include steelmaking, heat treating, and finishing operations such as phosphating, acid cleaning, electroplating, welding, and hot dip galvanizing. Hydrogen from these sources is often termed "process hydrogen," or "internal hydrogen." For purposes of this appendix, crack growth caused by hydrogen from these sources is referred to as internal hydrogen embrittlement (IHE).

In the case of galvanized steel fasteners, the main source of internal hydrogen is pickling, the removal of heat treatment oxide scale by immersion in hydrochloric or sulfuric acid solutions. During pickling hydrogen is deposited on the steel surface, some of which may be absorbed into the steel. Hydrogen from this source can be minimized by use of pickling inhibitors, or avoided by mechanical descaling, such as grit blasting.

Another potential source of hydrogen during the galvanizing process is release from internal trap sites during heating in the molten zinc bath. Most of the hydrogen contained in steel resides in a combined, or trapped, form. Trap sites may include non-metallic inclusions, carbide particles, grain boundaries, vacancies, and dislocations. In the trapped state, hydrogen is unable to diffuse, and it is considered to be innocuous. However, when steel is heated during the galvanizing process, some hydrogen atoms are released from trap sites, and become dissolved in the steel. The dissolved atomic hydrogen is able to diffuse and cause embrittlement. Atomic hydrogen released from traps during galvanizing is prevented from leaving the steel by the zinc coating, which serves as a barrier at the surface. Some of the newly released hydrogen remains in the dissolved state if the steel is rapidly cooled to room temperature after galvanizing. Dissolved hydrogen from this source may lead to IHE when the steel is subsequently exposed to sustained tensile loading. Release of atomic hydrogen from trap sites during galvanizing was first reported in 1975 [10], and later confirmed by Brahimi [11], who referred to the phenomenon as "up quenching." The amount of hydrogen from this source can be significant in the case of steels that are tempered at temperatures below that of the hot-dip galvanizing bath. However, A354 BD rods are generally tempered at significantly higher temperatures than a galvanizing bath, so that IHE from this source is minimal.

**Environmental Hydrogen** -- Hydrogen can also enter steel from the environment as a result of cathodic protection, exposure to hydrogen gas, or corrosion in water. Hydrogen from these sources is generally called "environmental hydrogen." When hydrogen enters steel by a corrosion process, it is sometimes called "corrosion hydrogen." For purposes of this appendix, crack growth from any of the external sources during service is referred to as environmental hydrogen embrittlement (EHE). In the case of high-strength steels undergoing corrosion in an aqueous environment, EHE is also referred to as stress corrosion cracking (SCC).

Of particular interest for galvanized A354 BD rods is EHE resulting from the deposition of hydrogen on steel as a result of galvanic corrosion.

Galvanic corrosion occurs when dissimilar metals are in electrical contact and immersed in a corrosive environment. In the case of galvanized steel, galvanic corrosion takes place when steel is exposed at breaks in the coating under wet conditions. When this happens, zinc becomes the anode of a galvanic cell that sacrifices itself to protect the exposed steel from corrosive attack. At the same time, hydrogen is deposited on the exposed steel, which acts as a cathode.

Figure 1 is a potential-pH, or Pourbaix, diagram [12], which provides a succinct compilation of thermodynamic data for iron, its oxides, and water. As such, it is a convenient framework to show what is possible when steel and zinc are exposed to water.



Figure 1. Potential-pH Diagram for the Iron-Water System, Showing the Corrosion Potentials of Steel and Zinc in Water, and the Region of Water Stability Between Dotted Lines a and b.

Stability limits for water are also shown as dotted lines. Above the upper dotted line, water can decompose to form oxygen. Below the lower dotted line, water can decompose to form hydrogen. Between the dotted lines, water is thermodynamically stable.

When steel is exposed to air-saturated water, its potential and the pH of the water are typically located at the point plotted in the corrosion region at a pH of about 6, and an electrode potential of -0.70 volts, measured against a saturated calomel electrode (SCE). The electrode potential of a zinc coating corroding at this pH is -1.06 volts (SCE), and it is located in the immunity region of iron. When the two metals are coupled together, and the area of zinc is large compared to that of the steel, as is the case when steel is exposed at a void in a galvanized coating, the potential of the steel is pulled to that of zinc, and into the domain where it is immune to corrosion.

When the electrode potential of the steel surface is pulled below the lower stability limit of water, hydrogen can be deposited as the water is decomposed. Thus, the thermodynamics are favorable for production of hydrogen on steel exposed at breaks in a zinc coating in an aqueous environment.

The electrochemical reactions involved in the generation of hydrogen during the sacrificial protection of steel by a zinc coating are shown below in simplified form, and shown on Figure 2.

Zinc in the galvanized coating acts as the anode of a galvanic cell, with the dissolution of zinc to form zinc ions in solution and release of electrons to the metal,

$$Zn \rightarrow Zn^{+2} + 2e^{-2}$$

Steel exposed at breaks in the galvanized coating acts as the cathode, with the reaction of water and electrons to form hydroxyl ions in solution, and hydrogen, some of which is absorbed by the steel.

$$2e^{-} + 2H_2O \rightarrow 2OH^{-} + H_2$$

Dissolved zinc from the anode and hydroxyl ions from the cathode react to form zinc hydroxide precipitate, generally known as white rust.

$$Zn^{+2} + 2OH^{-} \rightarrow Zn(OH)_2$$
 (white-rust precipitate)



Figure 2 – Reactions That Occur During Sacrificial Corrosion of Galvanized to Protect Steel Exposed at Bare Spots with the Deposition of Hydrogen.

The overall chemical reaction, obtained by taking the algebraic sum of the partial electrochemical reactions, is

$$Zn + 2H_2O \rightarrow Zn(OH)_2 + H_2$$

Oxygen can also react at the steel surface without the formation of hydrogen, according to:

$$2e^{-} + \frac{1}{2}O_2 + H_2O \rightarrow 2OH^{-}$$

a competing process that reduces the rate of hydrogen evolution. For this reason, restricted access to oxygen in crevices, such as within a thread engagement or a crack, favors the deposition of hydrogen.

#### 3. Susceptible Steels

In general, susceptibility of steel to hydrogen embrittlement varies with composition, microstructure, and strength level. For example, stainless steels with an austenitic microstructure are extremely resistant to hydrogen embrittlement. Cold-drawn steels with an elongated pearlitic microstructure are resistant under normal atmospheric conditions at high strength levels.

A354 BD rods are generally made from AISI 4140, a medium-carbon, low-alloy (Cr-Mo) steel that is heat treated by austenitizing, quenching, and tempering to produce a tempered martensite microstructure. The tempering temperature controls the strength of this material. Strength level can be described in terms of yield strength, ultimate tensile strength, or hardness. In the case of A354 BD rods, these properties are well correlated, and for purposes of this appendix, strength is discussed in terms of hardness.

Generally, as hardness increases, resistance of AISI 4140 to hydrogen embrittlement decreases. A critical strength or hardness limit for the onset of susceptibility depends a variety of factors including: 1) intensity of the hydrogen source, 2) type of loading, and 3) geometry of the steel part. Other factors, such as impurity content, also have been shown to affect susceptibility in similar alloys [4].

## 4. Sustained or Slowly Increasing Tensile Load

When high-hardness, susceptible steel is placed under a tensile load, time is required for hydrogen to diffuse to planes of weakness. As a result, conventional mechanical tests, such as tensile and impact tests are generally too fast to allow for diffusion of hydrogen; thus they are insensitive to the effects of hydrogen. To detect hydrogen embrittlement, it is necessary for tensile loads to be maintained for sufficient time to allow diffusion of hydrogen to planes of weakness to support slow crack growth.

For a given steel in a particular environment, it is generally accepted that there is a critical level of load, or threshold, required for hydrogen embrittlement. This threshold is determined by the thermodynamic activity of the hydrogen. In the case of IHE, the activity is related to the concentration of hydrogen dissolved in the steel. For EHE in gaseous environments, the activity depends on the partial pressure of hydrogen. For EHE in a corrosive aqueous environment, the activity depends on the electrode potential at the surface.

Threshold loads are often determined by loading a group of test specimens to different levels, and waiting for a sufficient length of time to see which loads resulted in failure, and which did not. In 1975 [10], it was shown that thresholds can also be determined by very slow application of load until the onset of crack growth is detected.

## 5 - Previous Studies of the EHE of 4140 Bolt Material

In 1973, Boyd and Hyler [9] reported the results of a large research study on the hydrogen embrittlement of high-strength bolts that was conducted for the Research Council on Riveted and Bolted Structural Joints. This work included A325 (HRC 25 to 34) and A490 (HRC 33 to 39) bolts, both with and without hot dip galvanized coatings. These bolts were loaded by the turn-of-the-nut method and exposed to corrosive conditions in laboratory and outdoor environments. No failures were reported for uncoated or galvanized A325 bolts, or for black (uncoated) A490 bolts. However, numerous failures were found among the galvanized A490 bolts.

Based on the above, Boyd and Hyler suggested that the galvanized A490 failures were due to EHE resulting from a combination of the higher hardness of A490, and hydrogen produced by galvanic corrosion of the zinc coatings.

To further explore the effects of galvanizing and hardness on hydrogen embrittlement of A490 bolt material, Townsend [10] conducted fracture mechanics tests of black and galvanized bars according to ASTM E1681, see Figure 3.



Figure 3 - Cantilever Bend Testing of Pre-Cracked Cantilever Beams According to ASTM 1681.

Precracked, quenched-and-tempered 4140 steel bars with hardness in the range 33 to 49 were subjected to rising step load in cantilever bending in three different ways as follows:

• Loading at normal test speeds in air to determine a baseline value of fracture toughness, labeled as Kx on Figures 4 and 5.

- Slow loading (0.2 KSI-in<sup>1/2</sup>) in air to determine the IHE threshold, labeled Kh on Figure 4 (Dry Test)
- Slow loading in 3.5% NaCl solution to determine the EHE threshold, labeled as Ksc in Figure 5 (Wet Test)



Figure 4. IHE tests - Dry-test threshold stress intensity factors, Kh, for slow loading of galvanized bars in air compared to Kx for fast loading in air [10]. Open circles – Fast fracture Kx for all surfaces; Crossed circles – hot-dip 55% Al-Zn; Blue triangles – hot-dip zinc; Yellow squares – electroplated and baked zinc.



Figure 5. EHE Tests - Wet-Test threshold stress intensity factors, Ksc, for slow loading in water compared to Kx for fast loading in air [10]. Open circles – Fast fracture for all surfaces; Crosses – no coating; Black circles – hot-dip 55% Al-Zn; Blue triangles – hot-dip zinc; Yellow squares – electroplated and baked zinc.

The results of these tests conducted with fatigue-precracked, fracture-mechanics specimens led to the following conclusions.

- Threshold loads for IHE of zinc and zinc alloy-coated 4140 steel decrease with increasing hardness
- Threshold loads for EHE of zinc and zinc alloy-coated 4140 also decrease with increasing hardness

- Threshold loads for EHE of zinc and zinc alloy-coated 4140 are significantly less than that of bare steel, owing to the increased hydrogen activity resulting from galvanic corrosion of the coating
- Threshold loads for EHE of zinc and zinc alloy-coated 4140 are also significantly less than the IHE thresholds, showing that EHE is a significantly greater potential threat than IHE.

As shown on Figure 5, the EHE thresholds of galvanized steel decrease from 58 to 20 KSI-in<sup>1/2</sup> as the hardness increases from 30 to 40 HRC. This is equivalent to an average 6.6% reduction in threshold load for each HRC unit increase in hardness.

This work also showed that the electrode potential of bare steel in 3.5% NaCl solution is -0.70 Vsce, and that of galvanized steel is -1.06 Vsce. As shown in Figure 5, this is accompanied by a decrease in EHE threshold from 87 to 38 KSI-in<sup>1/2</sup>. This is equivalent to an average decrease of 0.16% in threshold load for each mv change in electrode potential.

## 6. Crack-Growth Rates

As discussed, for example by Brown (8), EHE crack-growth rates in pre-cracked, high-strength steel depends on stress intensity factor ( $K_1$ ) as shown in Figure 6. Below the threshold stress intensity factor, KIt, cracks do not grow. Above KIt, there are three regions of crack growth:

- Stage I crack growth begins just above the EHE threshold, Kit, and increases rapidly with increasing  $K_{\rm I}$
- Stage I is followed by Stage II in which the rate of crack growth is independent of K<sub>I</sub>. It is believed that Stage II crack growth is limited by the diffusion rate of hydrogen to planes of weakness within the plastic zone just ahead of the crack tip
- Stage III occurs when K<sub>1</sub> approaches K<sub>Ic</sub>, and crack growth changes from slow EHE crack growth to rapid ductile tearing.



Figure 6. Three Stages of EHE Crack Growth

In 1975 [10], EHE crack growth rates averaged over the three stages of EHE in galvanized 4140 steel with hardness of HRC 35 to 39 were estimated to be in the range of 10 to 20 mils per hour.

# 7. Application of Pre-Cracked Fracture Mechanics Data to Full-Size Threaded Rods

Results discussed in the preceding section were obtained by use of fatigue precracked, fracture mechanics specimens, and expressed in terms of plane-stain values of Ksc. A key question is whether these values of Ksc can be applied to threaded rods that do not have an intentional pre-crack. For this to be so, two criteria must be satisfied: 1) a crack must be present, and 2) the crack must be long enough to meet the requirements for conditions of plane strain.

Hot-dip galvanized coatings on anchor rods are typically comprised of brittle ironzinc intermetallic compounds, which easily crack during tensioning. When rods are tensioned, they eventually undergo localized yielding at thread roots where they are engaged with a nut, thus causing the coating cracks to open, and producing two important effects. The first effect is exposure of steel at the thread root, and creation of a galvanic cell, which produces hydrogen. In terms of the electrochemical deposition of hydrogen, creation of a fresh steel surface at the crack root is particularly significant because the atomically clean steel surface is highly reactive for cathodic deposition of hydrogen. Moreover, when steel at the thread root is stressed above the yield point, the rate of hydrogen deposition and permeation are further accelerated [13].

The second effect results from the fact that hot-dip galvanized coatings are metallurgically bonded to the steel, so that a crack in the coating can be considered as if it were a crack in the steel.

Although the crack in a galvanized coating can be no greater than the thickness of the coating itself, typically about 0.005 inch, the actual length of a crack at a thread root is equal to the sum of the coating thickness plus some fraction of the thread depth. The maximum possible crack length would be the coating thickness plus the entire thread depth. In the case of a 3-inch-diamenter, coarse-threaded rod, this would be equal to 0.005 + 0.136 = 0.141 inch.

According to ASTM E399 [14], one of the criteria for plane strain conditions is that crack length must exceed the value  $2.5(K_1/YS)^2$ , where  $K_1$  is the stress intensity factor, and YS is yield strength.

Using the values of  $K_{sc} = 40$  KSI-in<sup>2</sup>, and YS = 140 KSI, the minimum crack length for plane strain is 0.204 in. Thus, the cracks in the galvanized coating do not meet the requirements for plane strain, and one must conclude that the values of  $K_{sc}$  determined by testing fatigue pre-cracked specimens under plane-strain conditions do not apply to threaded rods at the strength level of A354 BD. In the absence of plane-strain, the threshold K will vary according to size and geometry, and will be significantly higher than threshold K values determined under plane-strain conditions.

Moreover, Olsen [15] reviewed five equations that have been proposed for calculation of stress intensity factor, K<sub>1</sub>, for threaded rods with a pre-existing crack. These equations are generally of the form,

$$K_{I} = \sigma Y(a/D)(\pi D)^{1/2}$$

where

σ= stress

Y(a/D) = a geometric factor usually expressed as a 5<sup>th</sup> order polynomial

a = crack length

D = major diameter of the threaded rod

Olsen showed that these solutions converge at longer crack lengths, but for small cracks, the values of Y(a/D) varied over a range of 0.6 to 3.3. This leads to the conclusion that further research is needed before fracture mechanics can be applied to threaded fasteners with small cracks.

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