



Hydrogen Embrittlement in Coated Steel Fasteners

A review of the literature

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High strength threaded steel fasteners (tensile strengths greater than 160,000 psi) are known for their susceptibility to hydrogen embrittlement (HE) failure, yet their strength is needed for critical applications such as bridges, vehicle engines, aircraft and ships. The prevention of HE in these components is an important concern for joint designers, fastener manufacturers and application engineers. This is particularly true with respect to the selection and application of metallic coatings. These coatings extend the corrosion life of the fastener; but they can also cause delayed HE failure.

In a previous paper, the mechanisms of hydrogen damage, diffusion, transport and trapping were reviewed. Also reviewed were the analytical techniques used for measuring the susceptibility of steels in particular. The primary purpose of this review is to discuss the topic of metallic coatings and their role with respect to hydrogen embrittlement of fasteners. To achieve this, the topic was divided into sub components. First, the electrochemistry of hydrogen generation and absorption in metals will be reviewed. This will be followed by a discussion on analytical methods used to measure hydrogen content and hydrogen permeability of metals. Third, a number of coating processes will be reviewed with respect to the role of surface properties on hydrogen absorption and effusion, and their impact post exposure heat treatment (baking) for reducing susceptibility. Finally, the standard ASTM test method for quantifying HE resulting from processes (coating, baking, etc.) will be reviewed in detail.

What became apparent in the process of this review was that, given what is known, industry standards have not adequately addressed the prevention of hydrogen

embrittlement from coating processes. There has also been a lack of consistency in preventive approaches. Some specifications prohibit the application of high risk coatings such as electroplating or hot dip galvanizing. In some cases coating process limitations are specified, such as the use of inhibited acids for pickling. In other cases baking and HE testing is required. Yet the specified bake times may not have the desired effect, and specified test methods may lack the necessary sensitivity to effectively detect embrittled parts. This situation has been slowly changing with the introduction of a new ASTM test method in 1999. ASTM F1940 prescribes a standardized methodology for using the incremental step load (ISL) method for monitoring fastener coating processes for the risk of HE. The test method is also beginning to be used for research purposes to investigate ways to optimize coating and baking processes. In the meantime it remains a powerful tool that can be readily used for process control purposes.

Hydrogen Generation Mechanisms

Hydrogen assisted failures are divided into two broad categories based on the source of hydrogen, 'environmental' and 'internal'. Environmental hydrogen embrittlement (EHE) occurs when the installed fastener is exposed to hydrogen resulting from service conditions, such as corrosion or hydrogen rich atmospheres. Stress corrosion cracking (SCC) falls into this category. Internal hydrogen embrittlement (IHE) is caused by residual hydrogen resulting from processing conditions, either during steelmaking or during coating operations. The processing history of a fastener is the

primary determinant as to whether delayed internal hydrogen embrittlement failure will occur once the fastener is statically or dynamically loaded.

The discussion that follows will focus on the electrochemical sources of hydrogen. From an electrochemical perspective there are two broad hydrogen generation mechanisms for steel fasteners. (i) Hydrogen generated as a result of corrosion, and (ii) hydrogen generated during electroplating. Corrosion of the metal can occur either during surface cleaning and pickling of the fastener prior to coating (internal), or in-service from contact with an electrolyte such as salt water or acidic media (environmental). An additional source of corrosion generated hydrogen is hydrogen generation by galvanic protection, otherwise known as cathodic hydrogen absorption (CHA).

The potentially damaging effects of ‘internal’ hydrogen absorbed during plating or cleaning can be reversed by a post-plate heat treatment referred to as baking. The topic of baking effectiveness will be expanded later; however it should be noted that an often cited misconception is that of ‘de-embrittlement’ by baking. Hydrogen embrittlement phenomena or more specifically hydrogen damage occurs in the presence of stress that exceeds the HE threshold of a given material, (once the fastener is under load). Baking does not reverse such damage; however under certain conditions, it can render hydrogen that is in the metal lattice less harmful by either causing it to migrate to internal trap sites, or by expelling it from the lattice altogether.

Mechanism of Corrosion

Corrosion will cause the oxidation and dissolution of a metal into a corrosive solution. A corrosive solution can either be present locally as is typical in environmental corrosion or can immerse the metal as with acid pickling. The same corrosion mechanism applies to a coated fastener or an uncoated fastener, the difference being the metal that is oxidized. The overall reactions with say a hydrochloric acid solution are



or



These reactions can be simplified and expressed as half cell reactions. The anodic reaction is



while two cathodic reactions are prevalent, the reduction of dissolved oxygen to produce hydroxyl ions,



and once the dissolved oxygen is depleted, the reduction of hydrogen ions to produce first atomic hydrogen which can diffuse into the metal and then molecular hydrogen.



Mechanism of Electroplating

Electroplating is a cathodic deposition process. The plating solution contains metallic chlorides and other salts, rendering it conductive and rich with the metal to be plated. The fasteners serve as cathode (negative terminal) and the metal to be coated serves as anode (positive terminal). Take the example of zinc electroplating (the same basic reactions would apply for the electrodeposition of any other metal). When the electric circuit is closed, the cathode becomes negatively charged and zinc ions in solution migrate towards it, diffuse through the cathode film, and plate out as a zinc coating.



Meanwhile at the anode, zinc atoms oxidize by giving up electrons and dissolve into the electrolyte as zinc ions. This essentially maintains the zinc concentration in the electrolyte. Electrons given up by the zinc atoms will flow to the cathode via the power supply.



If zinc ions are not readily available for the electrons at the cathode, water is reduced to produce hydrogen ions and hydroxyl ions. Hydrogen ions can in turn be reduced to form atomic hydrogen which can diffuse into the coating and base metal, and molecular hydrogen which bubbles into the plating bath.



Faraday's Law of electrolysis relates the mass of coating substance produced at an electrode during electrolysis to the number of moles of electrons (the quantity of electricity) transferred at that electrode.

$$m = \frac{Q}{qn} \cdot \frac{M}{N_A} = \frac{1}{qN_A} \cdot \frac{QM}{n} = \frac{1}{F} \cdot \frac{QM}{n} \quad (10)$$

Where

m = mass of the coating substance produced at the electrode, g,

Q = total electric charge that passed through the solution, C,

q = electron charge = 1.602×10^{-19} C per electron,

n = valence number of the coating substance as an ion in solution (2 for zinc),

F = Faraday's constant, $96,485 \text{ C} \cdot \text{mol}^{-1}$,

M = molar mass of the coating substance, g per mole (65.38 for zinc), and

N_A = Avogadro's number = 6.022×10^{23} ions per mole.

In practice, the total charge Q is calculated by integrating the electric current $I(t)$ over time t :

$$Q = \int_0^T I(t) \cdot dt \quad (11)$$

where T is the total amount of time of the electrolysis. In the simple case of constant current electrolysis:

$$Q = I \cdot t \quad (12)$$

The “cathode efficiency” of a plating bath is a measure of the percentage of the applied current being utilized for depositing the coating substance. For example, cathode efficiency for an acid-chloride zinc bath is roughly 90%. When using Faraday’s law to determine the theoretical coating weight of zinc, 90% of the applied current must be taken for I in Equation 12. Conversely, current not being used for plating generates hydrogen by Equations 7 and 8. Therefore as a general rule, high efficiency baths generate less hydrogen than low efficiency baths, which means that they are also better for minimizing the risk of IHE.

The “current distribution” is the ratio of current density at a point X to the average current density on a workpiece as it is being plated. Geometry of the workpiece is the principle factor affecting current distribution. For example, the current density at the centre of a *long* bolt can be several times lower than at the ends. This effect becomes more pronounced as bolt length increases and diameter decreases. The result is what is known as the “dog bone effect”, where the coating thickness at the centre is proportionally lower than at the ends. The dog bone effect can cause severe problems with thread fit when plating long bolts, since meeting the minimum required coating thickness at the centre invariably results in excessive coating thickness at the threaded end. Another example of the effect of geometry on current distribution is with a *recess* such as the socket of an *internal drive* screw. Low current density inside the recess as compared to the rest of the screw makes it notoriously difficult to coat adequately. Aside from the geometric effect, the difference between high and low current density locations is increased with increasing plating current. One important consequence of this is that more efficient

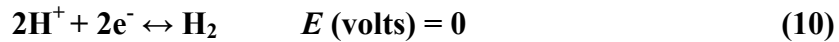
plating processes such as acid-chloride zinc baths also exhibit poorer current distribution than a lower efficiency alkaline zinc bath.

The “throwing power” of a plating bath is a measure of the bath's ability to overcome the effect of poor distribution by delivering more uniform coating thickness between the high and low current density areas of the workpiece. Since it is a function of current distribution, throwing power deteriorates with more efficient baths. However, in today's world of surface finishing, many proprietary bath formulations have been developed to improve throwing power for each type of plating process by influencing the localised conductivity of the solution. Electroplated coating standards for fasteners are specified in ASTM F1941.

Electrochemistry of Hydrogen Generation

In order to further understand the mechanisms of hydrogen generation and absorption, a review of elementary electrochemistry is necessary.

Consider the following reaction on a platinum electrode.



As is shown later in Table 1, this reaction has an electrode potential E° (oxidation potential) of zero. When this reaction is at equilibrium, the rate of oxidation equals the rate of reduction, resulting in zero net current. The magnitude of the current generated by the electron flow in either direction is called the exchange current density, i_o . It is defined as the electrochemical equilibrium rate constant and is a

measure of the kinetic properties of a particular electrode material. It follows that the electrode potential E for Reaction (10) is equal to the equilibrium potential E^o .

A net surface reaction rate can cause a potential change from the equilibrium resulting in a net current flow. This is called polarization (or overpotential) and is defined by

$$E - E^o = \eta \text{ (overpotential).} \quad (11)$$

For cathodic reactions, the electron-rich electrode moves the surface potential to the negative direction; hence η is negative by definition. For anodic reactions, for which electrons are removed from the electrode surface, η is positive. There are two types of polarization; activation and concentration polarization; and they can determine the reaction rate. Activation polarization η_{act} is the kinetically produced overpotential corresponding to the transfer of charges at the electrode. It is a function of current density i and is given by

$$\eta_{act} = \beta \log \frac{i}{i_o} \quad (12)$$

where β is the Tafel constant for the half cell reaction. When transfer of charges determines the reaction rate, the reaction is said to be under activation control.

Concentration polarization η is a change in potential caused by the depletion of the layer of ionic species next to the electrode (diffusion layer) and is a function of mass transfer. In reaction (4) if dissolved oxygen in the solution adjacent to the

electrode surface is depleted, the reaction rate is determined by the rate of diffusion of dissolved oxygen from the bulk solution to the surface of the electrode. In this situation, a concentration gradient of oxygen exists in the solution and the potential change is referred as concentration polarization which can be calculated by

$$\eta_{conc} = \frac{-2.3RT}{nF} \log \frac{P_{H_2}}{[H^+]^2} \quad (13)$$

Where

R = gas constant, 8.31 J/mol · °K,

T = temperature, °K,

n = number of equivalents exchanged (2 for oxygen),

F = Faraday's constant, 96,485 C mol⁻¹,

P_{H₂} = hydrogen gas partial pressure, atmosphere,

[H⁺] = concentration of hydrogen ions, molecular.

The limiting current density i_L occurs when the diffusion rate of the reactive ions (oxygen in this case) to the diffusion layer has reached its limit. No increase in overpotential can change this condition. i_L is given by

$$i_L = n F D C_b \delta \quad (14)$$

where

D = diffusivity of reacting species (oxygen),

C_b = bulk concentration of reactive species (oxygen), mol/m³,

δ = diffusion layer thickness, m.

Note: i_L can be increased by higher solution temperature, which accelerates diffusion and reduces δ .

Total cathodic polarization is the sum of activation and concentration polarization; whereas for anodic reaction, in which the metal electrode provides ‘unlimited’ reactant to be dissolved, concentration polarization is usually minor. Figure 1 schematically shows the sum η_{act} and η_{conc} contributions to total cathodic polarization. When i_o approaches i_L , diffusion takes over from activation to control reaction speed; therefore the total corrosion rate is limited by the diffusion of the oxidizer from the bulk solution. For iron and steel in dilute aerated salt solution, oxygen reduction (Reaction 4) is the major cathodic reaction (Deluccia [2]).

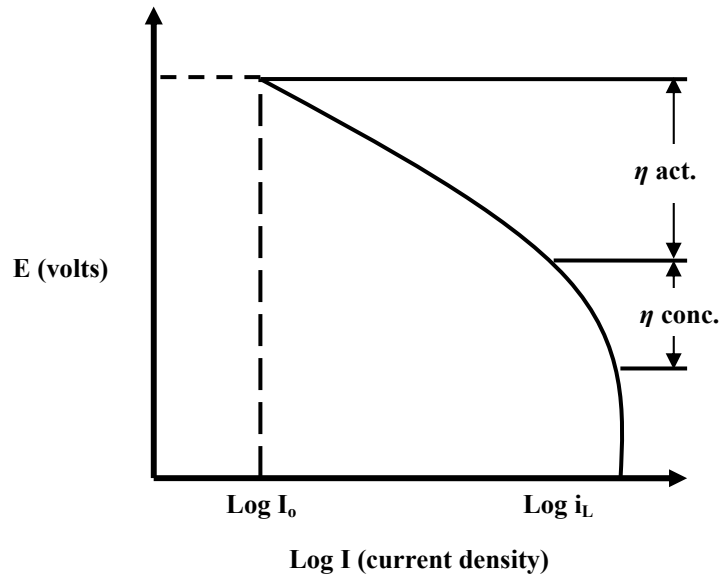


Figure 1: Generic example of combined activation and concentration polarization at cathode (source: [2] Fig. 2).

The concentration of hydrogen in solution is represented by the pH value. Therefore, the equilibrium potential for hydrogen reduction reaction (5) can be calculated by

$$E_{\text{H}^+/\text{H}}^0 = -0.0591 \text{ pH } (@298^\circ\text{K vs. SHE}). \quad (15)$$

In a neutral solution (pH 7) versus saturated calomel electrode (SCE 0.241V vs. standard hydrogen electrode, SHE), $E_{\text{H}^+/\text{H}}^0$ is $-0.655 \text{ V}_{\text{SCE}}$. Kinetics again adds an overvoltage or polarization, η for this reaction to proceed at a given rate:

$$E_{\text{H}^+/\text{H}}^0 = -0.0591 \text{ pH} - 0.241 + \eta (@298^\circ\text{K vs. SHE}) \quad (16)$$

For hydrogen reduction in NaCl solution with moderate reaction rate, concentration polarization can be ignored: thus the activation polarization or overvoltage for hydrogen evolution can be estimated by equation (12). The Tafel constant β will be given as -0.1V for this calculation [4]. What controls the value of overvoltage is the hydrogen exchange current density, i_o . Generally speaking the value of i_o on Fe is one to five magnitudes larger than those on the coating metals such as Cd, Zn, Sn, and Al. Therefore, the overvoltage for hydrogen evolution on those metals is much higher than that on iron. Consequently, it is more favourable for hydrogen to be generated on iron (and steel) surfaces (Zakroczymski [5]).

In reaction (5), atomic hydrogen results from the donation of an electron to a proton to form a hydrogen atom on the surface of electrode (e.g. steel): these hydrogen atoms may recombine to form molecular hydrogen that can accumulate and bubble off of the surface. However, before the hydrogen molecule is formed, there is

a considerable residence time during which the nascent hydrogen atoms can adsorb onto the metal surface and absorb into the lattice of steel. The rapidity of forming molecular hydrogen is affected by the catalytic properties of the electrode surface. A good catalyst (e.g. Pt or Fe) has a lower hydrogen overvoltage, while a poor catalyst (e.g. Hg) leads to a higher overvoltage. When hydrogen recombination inhibitors (or catalyst poisons), such as sulphur, arsenic, phosphorus, tin, and cyanide are present in the environment, hydrogen recombination is retarded, which promotes the ability of atomic hydrogen to enter the steel. On the other hand, poisons do increase the hydrogen overvoltage and may reduce the total reaction rate for the hydrogen evolution reaction (5) (Zakroczymski [5]).

Cathodic Hydrogen Generation by Galvanic Protection

For a coated steel fastener, the expected anodic reaction is the dissolution of the coating metal to produce ions in local solution, reaction (1). At the cathode reactions (4) and (5) apply. The two half-cell potentials from the anodic reaction and the cathodic reaction are different and they are not allowed to coexist separately on the electrically conductive surface. Each of them has to polarize to a common intermediate oxidation potential E^o .

Metallic coatings such as zinc based coatings are used because their oxidation potential is more negative than that of steel, meaning they have a higher propensity for corrosion. Why does this happen? Zn and Fe will develop their own corrosion potentials when immersed separately in dilute acid solution. Zinc, whose E^o is more negative, tends to generate electrons which are transferred to the more positive iron.

In this galvanic couple, zinc becomes the anode and the dissolution of zinc has its rate increased. On the contrary, the more noble iron has the rate of its dissolution decreased due to the excess of electrons drawn from zinc. Therefore, iron is the cathode of the cell. Decreasing the corrosion rate of one metal (iron) by coupling it to a sacrificial anode (zinc) is the basis of cathodic (galvanic) protection.

For a coated steel fastener, the anodic activity of the coating is responsible for galvanic protection. This sacrificial nature makes zinc based coatings very effective for protecting steel fasteners against corrosion. Yet this very characteristic can be an additional source of hydrogen that is cathodically generated at the base metal in a corrosive environment, and can precipitate the onset of hydrogen assisted cracking.

A prerequisite for cathodic hydrogen absorption (CHA) is that the coating must be either damaged or consumed as a result of corrosion. Townsend [6] and others have demonstrated this with fatigue pre-cracked test specimens immersed in conductive solutions while being loaded. In a variation of this theme Pollock and Grey [7] observed the impact of CHA on high strength 4340 steel that was coated with a porous cadmium coating and subsequently immersed in paint strippers (organic solvent). In this case it was the porosity of the coating; not mechanical damage or corrosion; that provided access to the base metal for creating a galvanic cell.

It follows that by using a less active metal, alloy or multiphase system as protective coating, it is possible to avoid or reduce cathodic hydrogen generation in

the corrosive environment. Table 1 shows the standard oxidation potentials of a number of common metals.

Table 1: Standard oxidation potentials of metals at 25°C. (Source: [1])

Oxidation (corrosion) reaction)	Electrode potential* (E°)		
$\text{Au} \rightarrow \text{Au}^{3+} + 3\text{e}^-$	+ 1.498	↑	More cathodic: (less likely to corrode)
$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$	+ 1.229		
$\text{Pt} \rightarrow \text{Pt}^{2+} + 2\text{e}^-$	+ 1.200		
$\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$	+ 0.799		
$4(\text{OH}^-) \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$	+ 0.401		
$\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$	+ 0.337		
$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	0.000		
$\text{Pb} \rightarrow \text{Pb}^{2+} + 2\text{e}^-$	- 0.126	↓	More anodic: (more likely to corrode)
$\text{Sn} \rightarrow \text{Sn}^{2+} + 2\text{e}^-$	- 0.136		
$\text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e}^-$	- 0.250		
$\text{Co} \rightarrow \text{Co}^{2+} + 2\text{e}^-$	- 0.277		
$\text{Cd} \rightarrow \text{Cd}^{2+} + 2\text{e}^-$	- 0.403		
$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$	- 0.440		
$\text{Cr} \rightarrow \text{Cr}^{3+} + 3\text{e}^-$	- 0.744		
$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$	- 0.763		
$\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$	- 1.662		
$\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$	- 2.363		
$\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$	- 2.714		

*Relative to standard hydrogen electrode

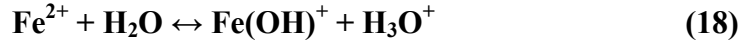
Electrochemical Conditions at Crack Tips

Studies into the electrochemical reactions that occur in occluded areas such as crevices and pits have revealed that localized conditions can differ substantially from those in the bulk solution. The geometrical constraints posed by localized topography of a pit or crevice prevent mixing with the bulk solution. Therefore it cannot be assumed that the production of nascent hydrogen cannot occur in neutral or alkaline environments. In fact there is a tendency for lowering of pH in these areas (Deluccia

[2], Zakroczymski [5]). In one of a number of studies on this topic, Smith, Peterson and Brown [8] conducted experiments in bulk 3.5% sodium chloride (NaCl) with varying acidity ranging from pH 2 to pH 10. They observed that the pH at the advancing crack tip remained constant in the range of 3.5 to 3.9. They proposed that the anodic reaction



is followed by the hydrolysis of water as it becomes thermodynamically unstable



To maintain electroneutrality, Cl^- ions rush to the crack tip. The result is the formation of stable hydrochloric acid.



The continued crack growth observed during these experiments is an indication that nascent hydrogen is able to diffuse into the metal lattice from the crack tip.

Quantifying Hydrogen

In the quest quantify hydrogen and model hydrogen permeation in metals, a number of different methods has been developed. The following is a review of the most significant ones.

Electrochemical Permeation Technique

Most studies since the 1970's have utilized the electrochemical permeation technique developed by Devanathan and Stachurski in the mid to late 1960's as an alternative to manometric pressure measurement methods (described later), that lacked accuracy and reproducibility. The technique is a measure of hydrogen adsorption (at the surface) and mobility through the lattice of a metal, and has contributed a great deal towards a better understanding of adsorption, penetration and transport (by diffusion) kinetics (Brass et al. [27]). Electrochemical permeation measures mobile, diffusible hydrogen, and is not suited for alloys that form hydrides or contain irreversible traps, nor does it quantify transport phenomena related to dislocation movement (Tien et al. [9]). The technique is also limited in that hydrogen must be permeated through foils with limited thickness (Deluccia [2]).

In Deluccia's [2] description, the electrochemical permeation technique provides controlled generation and collection of hydrogen permeating through a metal foil by electrolytic charging (Figure 2). A potentiostat maintains anodic potential which electrochemically oxidizes the hydrogen that emerges through the foil on the extraction side. The current supplied by the potentiostat is a direct measure of the instantaneous flux of hydrogen in the metal as it exits the extraction side, which is given by Fick's first law of diffusion. This in turn can be related to a (linear or non linear) concentration gradient of absorbed hydrogen throughout the membrane.

$$\frac{J}{ZF} = -D \left(\frac{dC}{dX} \right)_{X=L} \quad (20)$$

Where

J = flux atoms/m² · s,

Z = number of electrons transferred,

F = Faraday's constant, 96,485 C mol⁻¹,

D = diffusivity of hydrogen, m²/s,

C = concentration of hydrogen, mol/m³,

X = distance from cathode interface, m,

L = thickness of sheet foil, m.

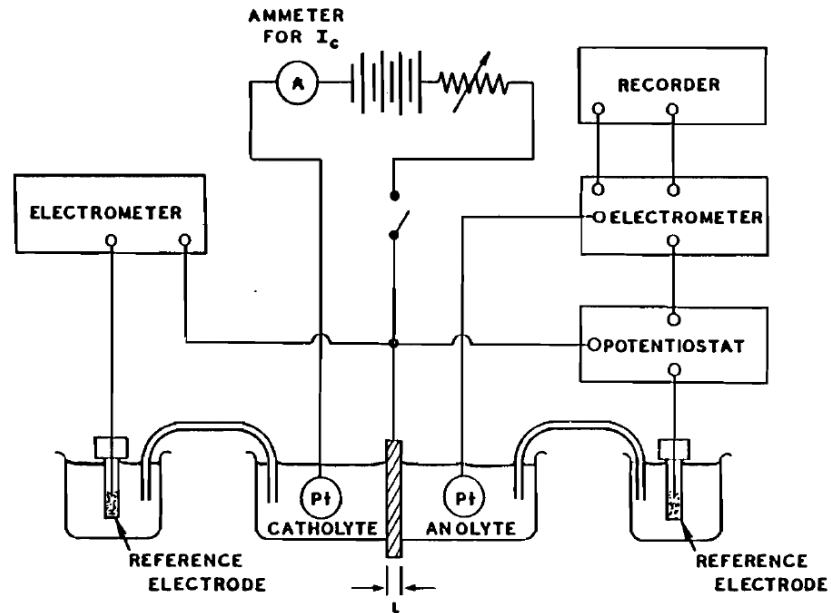


Figure 2: Electrochemical permeation cell. Can measure fluxes as small as 10⁻¹² g of hydrogen atoms/m²·s (Source [2] Fig. 5)

Barnacle Electrode Method

The Barnacle Electrode Method (BEM) is an adaptation of the electrochemical permeation technique that uses only the exit side of the permeation cell. More specifically the steel test foil or specimen is coupled with a nickel/nickel oxide electrode in an alkaline solution (Deluccia [2]). In this case it is the coupling that polarizes the specimen to a potential at which hydrogen is oxidized at the extraction side. BEM simplifies the experimental setup and is very sensitive. It is reported to be capable of measuring diffusible hydrogen concentrations in steels of less than 1 ppm. The test method was developed into an ASTM Test Method F1113 in 1987. In an attempt to address the problem of specimen thickness and relevance of the test to bulk material, Berman and Agarwala [10] varied the thickness of the specimen up to 6 mm and found good agreement with thin foils. This finding also demonstrated that the measurements are a function of bulk permeability rather than only surface permeability.

Another adaptation of the BEM technique known as the hydrogen patch cell which uses the same principle applied to measuring in-situ hydrogen penetration in steel. A particularly common application is for pipelines that carry hydrogen rich fluids [11].

Electrochemical Sensor

Mackor, Kreuk, and Schoonman [12] developed a novel electrochemical sensor for measuring mobile hydrogen concentration in a wide range of metals. The method

uses similar electrochemical principals, but adapted to a hand held sensor that makes it possible to sense hydrogen activity by measuring localized potential. The principal distinction between this and the previous methods is that measurements are made in a steady state condition on the specimen versus the hydrogen charged condition used in permeability testing. This makes it possible to map hydrogen concentration in a specimen without changing or disturbing its distribution.

The sensor is constructed on the principal of a concentration cell in which two different or equal metals are brought into contact with a liquid or solid electrolyte. The result is an asymmetrical M-M' or a symmetrical M-M cell as shown below. Measurements are based on the potential difference between the MH_x -electrolyte and MH_y -electrolyte interfaces when the sensor is placed of the test specimen. Figure 3 illustrates the sensor configuration and two prototype sensors.

MH_x	Electrolyte	MH_y
Sensing electrode	Liquid or solid	Reference electrode

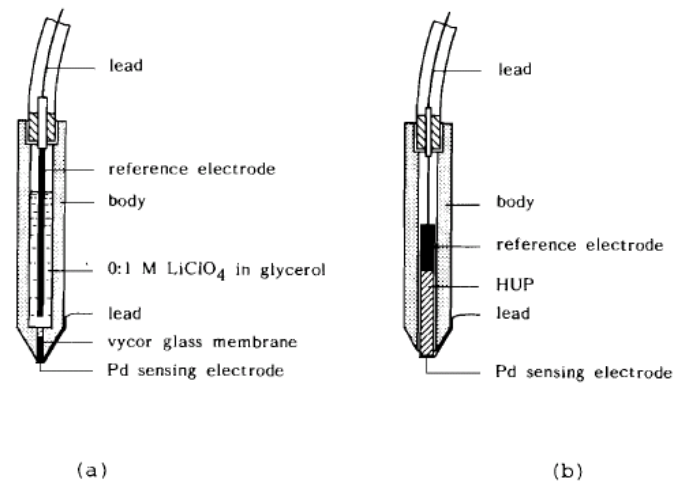


Figure 3: Electrochemical sensor (Source: [12] Fig. 2)

A considerable amount of work was conducted to determine the applicability of this technique to a variety of metals. With respect to steel it was found that the presence corrosion products and oxide layer can have a considerable impact on the measurements. A number of approaches were attempted to resolve this problem with varying degrees of success, however further work is required. If adapted to fastener type specimens, this test method might provide powerful analytical capabilities for mapping hydrogen activity of samples that are placed under load.

Manometric Pressure Measurement in Collecting Fluids

This technique involves the use of collecting fluids. In this approach a eudiometer is filled with a collecting fluid such as glycerine, liquid paraffin or mercury. The test specimen is allowed to degas in the eudiometer under temperature control, and the collected gas forms bubbles that collect at the top of the eudiometer. The volume of

gas is measured and is related to the weight of the specimen. This technique lacks accuracy and reproducibility and is highly dependant on the properties of the collecting fluid, which are all problematic in one way or another. Additionally the volumetric collection of gas is not always a function of hydrogen content alone, and this can lead to erroneous results. This technique is still used despite its shortcomings. These shortcomings led to the development of gas chromatography to reliably analyse the gas being collected.

Gas Chromatography

Quintana and Dannecker [13] used gas chromatography to measure the hydrogen extracted from weldments into a closed chamber. Welding is a recognized area for hydrogen assisted cracking. The technique is composed of three parts; (i) specimen preparation; essentially a steel plate on which a segment is welded. (ii) Degassing, whereby the welded specimen is allowed to degas in inert atmosphere into a closed, temperature controlled, test chamber. The degassing rate is accelerated by applying temperatures in the range of 150 °C for a period of about six hours. (iii) Analysis, whereby the quantity of hydrogen is measured using gas chromatography. The test method was shown to be very accurate and reliable. Suzuki et al. [14] adapted this test method for measuring diffusible hydrogen in high strength bolts. In this case the bolts were placed in a large enough chamber designed to accommodate their size. The results of hydrogen quantification were related to threshold stress testing under varying plating, baking and hardness conditions. The dual metric approach of quantification hydrogen and mechanically measuring threshold stress under varying

conditions is well suited for understanding the impact of trapping; reversible and irreversible, on diffusible hydrogen.

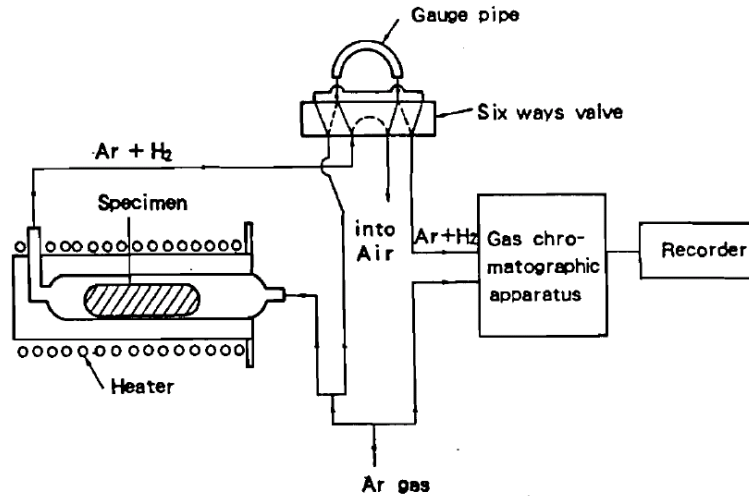


Figure 4: Electrochemical sensor (Source: [14] Fig 1).

Effects of Coatings and Surface Characteristics

A large number of studies have been conducted to determine the impact of various coatings on internal hydrogen embrittlement (IHE) of steel and fasteners. This section will address this topic from the perspective of hydrogen availability, notwithstanding stress and susceptibility, the other two ingredients for hydrogen assisted cracking. The topic can be divided into four broad categories. (i) The impact of surface preparation method on hydrogen absorption prior to coating. (ii) The impact of the coating process itself; e.g. electroplating generates cathodic hydrogen that is absorbed by the material. (iii) The role of coatings and surface characteristics as

barrier to hydrogen absorption and effusion. (iv) The effectiveness of baking as a process for hydrogen embrittlement relief following coating application. These four categories are often closely interrelated. However for the sake of a better distinguishing the phenomena related to coatings, they will be discussed separately.

Surface Preparation

Surface preparation is often an important prerequisite for coating. Most industrial processes use chemical media for surface preparation, such as alkaline degreasing, and acid pickling. This can be an important source of hydrogen resulting from the oxidation of the metal surface. A great deal has been done to minimize the hydrogen contribution from cleaning processes, starting with tight control of process parameters such as time, temperature, concentration, and the type of media (or acid) used. Another important development was the use of inhibitors that can limit the oxidation activity in an acid pickling bath, and also reduce hydrogen penetration. In a study on the prevention of HE by surface films, Murray [15] observed that inhibitors added to liquid media; such as during acid pickling; or in gas media, can occupy the surface area of the metal with a thin strongly bonded layer that alters the surface adsorption characteristics in a manner that effectively prevents hydrogen entering the metal.

An alternative to chemical cleaning has been the use of mechanical abrasion and descaling methods. This approach eliminates any contact with hydrogen altogether, but is sometimes problematic due to material handling issues.

Surface Characteristics

Surface properties and a coating's physical characteristics have an immense impact on the rate of hydrogen penetration. Pollock [16] conducted a detailed study on 4340 high strength specimens with a variety of electroplated coatings such as porous Cd, nonporous Cd, Brush Cd, Cd-Ti, and electroless Ni. Although the study does not isolate individual processing steps, such as surface preparation, plating and baking, one key conclusion was that the degree of embrittlement was a function of the porosity of the specific coating. This was illustrated by the lack of baking effectiveness with less porous coatings that tend to prevent hydrogen effusion. Another conclusion in this study was that the addition of brighteners in the plating bath appeared to lower the coating porosity.

In another study Pollock and Grey [7] applied porous cadmium plating to high strength 4340 steel specimens. They observed embrittlement following immersion of the specimens in paint strippers (organic solvent). In this case, the porosity of the coating provided access to the base metal for creating a galvanic cell and cathodic hydrogen absorption (CHA).

In his study on surface films, Murray [15] also demonstrated that the application of tungsten and non-metallic TiO_2 and Al_2O_3 thin films, in the order of 50 nm, is very effective in preventing hydrogen entry at the metal surface due to very low hydrogen permeability of the film. It is interesting to note that in 1970 a Canadian Patent was issued to Dingley and Rogers [26] that prescribed the application of an electroless thin copper layer (flash) before electroplating as a means

of minimizing hydrogen contact with the base steel. There is no information regarding the technical viability of this process, nor regarding its commercial viability for bulk fastener coating. The patent expired in 1987.

Surface properties of the metal also have an important role in hydrogen permeability. Murray [15] observed that thermally grown (at 1000 °C) adherent oxide films on stainless steel in the order of 100 nm can also have a barrier effect to hydrogen penetration. McCarty, Wetzel & Klobardanz [17] observed that carbonitriding of 1022 steel fasteners significantly lowered hydrogen permeability. These surface properties can block hydrogen absorption, but they can also reduce the effectiveness of baking.

Coating Process

This section will be preceded by a cautionary note. Most studies reviewed do not distinguish between the coating process and the hydrogen contribution of surface preparation. Acid pickling in particular can be a source of hydrogen that remains trapped during and after the subsequent coating step. With this caution in mind, we will review some of the most prevalent coating processes.

Many studies have found that plating is a high risk process with respect to IHE. As was discussed earlier, electrochemical reactions that occur in the process promote the adsorption and absorption of hydrogen. Depending on the porosity of the coating and its permeability to hydrogen, hydrogen charging is most elevated before the build-up of the coating layer, which acts as a barrier that slows down hydrogen

absorption, but can also trap hydrogen in the metal. Zinc, zinc alloys, nickel, chromium and cadmium¹ are the most common electroplated metal on fasteners. For the most part these coatings are fine grained with oriented atomic structures that make them less permeable to hydrogen, also making degassing more difficult. There are a great many formulations for plating processes, each with its own bath chemistry, brightness, efficiency, coating permeability etc. Therefore specific conditions will vary depending on the plating bath itself.

Voorhis [18] studied the impact of phosphate coating; a chemical conversion process in acidic medium; on the embrittlement of high strength military submunitions using the sustained loading at 65% of the fracture strength for 200 hours. He concluded that the process which takes place in a zinc-rich phosphoric acid bath does cause hydrogen embrittlement failure. However, baking at 90 °C for three hours, or natural degassing at room temperature for 30 days eliminated the problem. These findings have to be attributed to the porosity of the zinc phosphate coating. He also observed that better control of the zinc phosphate bath chemistry can reduce the degree of embrittlement. One area of weakness in this study is that the sustained loading method does not provide any reliable quantitative data on the degree of embrittlement because it does not measure threshold stress.

In his study on the effects of zinc coatings on stress corrosion cracking and hydrogen embrittlement, Townsend [6] confirmed that the galvanic nature of zinc

¹ Despite the elimination of cadmium coatings in commercial applications due the environmental concerns, these coatings are still prevalent in military applications. Efforts are underway as we speak by the military to find alternatives suitable for their applications.

coatings can be an additional source of cathodic hydrogen, as was discussed earlier. However, Townsend also made an interesting observation about hot dip galvanized (zinc) coatings. Despite fact that 'hot dipping' in molten zinc does not introduce any hydrogen, hot dip galvanized test specimens with a fatigue pre-crack exhibited a substantial drop in threshold stress, even in the absence of acid pickling. He postulated that internal hydrogen bound in trap sites was being released by the thermal energy of hot dipping, but prevented from escaping by the intermetallic coating layer. Brahimi [19] made the same observation in a similar study on hot dip galvanizing using the incremental step load method per ASTM F1940.

Mechanical plating and mechanical galvanizing applies a zinc coating by compaction of particulate zinc in a liquid medium filled with glass beads. From the perspective of HE avoidance, this process offers a number of advantages to zinc plating and hot dip galvanizing. First, the process is at room temperature, thus avoiding the thermal impact of hot dip galvanizing on hydrogen mobility. Second, since the process does not involve electroplating, there is no cathodic generation of hydrogen in contact with the metal being co-deposited. Hydrogen is evolved primarily from the reaction of the mildly acidic medium with the surface of the metal. This reaction occurs at a slower rate than during electroplating. The cold welding of relatively large zinc particles (~3-5 microns) does not tend to trap hydrogen gas during impaction. Third the coating itself is less dense and more porous than zinc plating or galvanizing. Fourth, the abrasive nature of mechanical galvanizing precludes the need for aggressive acid pickling. The metal surface is cleaned by the glass beads as the coating is being deposited (Brooks [20]).

Baking

The potentially deleterious effects of hydrogen absorbed during plating or surface cleaning can usually be eliminated by a baking heat treatment after processing. The potential severity of hydrogen damage is normally determined by the strength level or the amount of cold work within a fastener. Troiano [21] demonstrated that time to failure can be varied as a function of hydrogen content, or bake time. With baking, as interstitial (free) hydrogen content is reduced, the time to failure and the threshold stress increases. Baking has been shown to either expel hydrogen by effusion or cause it to migrate to stable trap sites, thus making it immobile (Townsend [6]).

The key factors that influence baking effectiveness are; (i) time, (ii) temperature, (iii) the permeability of the surface (coating, case, oxides, etc.), and (iv) material hardness. These factors result lead to a great deal of variability for effective baking conditions. Current industry practice calls for baking plated parts above 35 HRC for 4 hours at 190°C, within a few hours of plating. However, it has been shown in many studies that this is inadequate for truly susceptible parts. In some cases the baking is not really required, while in other cases bake times as long as 24 hours are necessary (Reddy et al. [22]), despite not being commercially viable. Robinson and Sharp [23] and others observed that in some cases, insufficient bake times can actually result in a lowering of threshold stress by releasing hydrogen from irreversible, innocuous traps, to the metal lattice, or to lower energy reversible traps. Until better guidelines are established, it is recommended that an effective baking schedule be primarily based on results of threshold testing and trial & error.

Standard Test Method for Process Qualification - ASTM F1940

Most of the studies in the literature have used some form of mechanical testing to measure fracture stress after plating and plating/baking combinations as the parameter for assessing the degree of embrittlement. Prior to the 1980's 200 hour sustained loading was the method of choice. There are many examples of the shortcomings of this approach. In an investigation into suspect cadmium plated high strength aircraft fasteners in the mid 1980's, Levy and Bruggeman [24] used sustained load testing to determine if parts were embrittled. They did not find any that failed the test, but this did not provide any assurance that parts were in fact not embrittled. The uncertainty compelled them to apply a costly baking process at 190°C for 48 hours to a very large volume of parts. In a 1988 study, Dreher [25] outlines not only the technical shortcomings of sustained load testing but also the practical difficulties in applying this approach for production quality assurance purposes.

Beginning in the late 1980's there was a clear emergence towards mechanical test methodology that utilized slowly increasing loading patterns, namely slow strain rate testing (SSRT) and incremental step load testing (ISL). These tests not only allow for the time-delay mechanisms of HE to evolve, but they do so while applying a very slow increase in stress/strain, that provides an accurate measure of threshold. In 1999 the incremental step load test method in ASTM F1624 was modified and adapted in ASTM F1940 to provide a methodology for quantifying the risk of internal hydrogen embrittlement (IHE) posed by coating processes. The test consists

of using a standardized specimen as a ‘witness’ by processing it with other production parts. By doing so, it is exposed to the same hydrogen charging conditions as the production parts. The test specimen is a standardized notched square bar (SQB) made of highly susceptible AISI E4340 steel heat treated to 50-52 HRC. In terms of HE susceptibility, this specimen can be useful to represent a worst case scenario. In other words production fasteners will never be more susceptible than the SQB specimens. Fastener product specifications for class 12.9 fasteners, which is the highest strength grade, set a maximum allowable hardness limit of 44 HRC.

ASTM F1940 also specifies a standardized test protocol with pre-defined load/strain increments and hold times. The SQB specimen is subjected to a sustained four-point bending load and slow strain rate under displacement control. The test indirectly quantifies the amount of residual hydrogen in the SQB specimen by measuring the threshold for hydrogen assisted cracking in an accelerated manner (≤ 24 h). The threshold is represented by the fracture load; called Notch Fracture Strength (NFS).

Bare (uncoated) SQB specimens are tested in the same manner to establish a ‘baseline’ NFS. The ratio of the threshold for each ‘witness’ over the baseline represents the percent Notch Fracture Strength (%NFS), which is another expression for the hydrogen susceptibility ratio H_{sr} .

$$NFS\% = \frac{NFS_{(W)F1940}}{NFS_{(B)F1940}} \times 100 \quad (21)$$

Where:

$NFS_{\%}$ = Percent Notch Fracture Strength

$NFS_{(B)F1940}$ = Notch fracture strength of bare SQB specimen

$NFS_{(W)F1940}$ = Notch fracture strength of coated SQB witness specimen

The $NFS_{\%}$ ratio, when statistically validated, represents the quantified risk of IHE from a coating process. ASTM F1940 establishes an acceptability limit which is equivalent to 85%². In other words a coating process that measures a $NFS_{\%}$ above 85% is not at risk of causing IHE, whatever of the susceptibility of the parts being coated. Such a process is considered to be safe (Raymond [28, 29, 30]).

The approach described in ASTM F1940 is a powerful tool that can be used to conduct empirical work and scientific research for examining the many factors that influence the risk of HE, including coating processes, coating process parameters, surface preparation and baking conditions.

² ASTM F1940 proposes an acceptability limit of 75% when $NFS_{\%}$ is calculated using the fast fracture strength of bare specimens as the denominator. This corresponds to roughly 85% when $NFS_{\%}$ is calculated as shown in Equation 1, where the baseline denominator is derived by subjecting bare specimens to the same incremental step load pattern used for the coated specimens.

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- . ASTM F1113 Standard Test Method for Electrochemical Measurement of Diffusible Hydrogen in Steels (Barnacle Electrode)
- . ASTM F 1624 Standard Test Method for Measurement of Hydrogen Embrittlement in Steel by the incremental Loading Technique.
- . ASTM F 1940 Standard Test Method for Process Control Verification to Prevent Hydrogen Embrittlement in Plated or Coated Fasteners.