Rupture and Fracture of Fastener by Embrittlement - Temper Embrittlement & Hydrogen Embrittlement

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1. Introduction

Embrittlement is a loss of ductility of a material, making it brittle. Embrittlement is used for any phenomena where a hostile environment compromises a stressed material's mechanical performance. Various materials have different mechanisms of embrittlement. Due to these various mechanisms, embrittlement manifests in a variety of ways, from slow crack growth to a reduction of tensile ductility and toughness. Often, cyclical stresses or environments lead to embrittlement.

Mechanisms of Embrittlement is a series complex mechanism that is not completely understood. The mechanisms can be driven by temperature, stresses, grain boundaries, or material composition. However, by studying the embrittlement process, preventative measures can be put in place to mitigate the effects. There are several ways to study the mechanisms. During metal embrittlement (ME), crack-growth rates can be measured.

The most common embrittlement findings for fastener in use or manufacturing should be as follows.

1. Work hardening of material to embrittlement on heading process, pinching process or threading process during fastener manufacturing; or
2. Material to be heat-treated with strength but with brittle characteristics and lack of toughness; or
3. Hydrogen embrittlement of hydrogen absorption on some metals and alloys during surface treatment manufacturing process such as it is happened in cathodes for electroplating; or
4. Stress corrosion cracking (SCC) is the embrittlement caused by exposure to aqueous, corrosive agent or atmosphere while fasteners serve in environment.

Work hardening, also known as strain hardening, is the strengthening of a metal by plastic deformation. These processes are known as cold working or cold forming processes. They are characterized by shaping the workpiece at a temperature below its recrystallization temperature, usually at ambient temperature. This strengthening occurs because of dislocation movements and dislocation generation within the crystal structure of the material. Such deformation increases the concentration of dislocations which may subsequently form low-angle grain boundaries surrounding sub-grains. Cold working generally results in a higher yield strength as a result of the increased number of dislocations and the sub-grains, and a decrease in ductility to embrittle the material of fasteners.

However, ductility of a work-hardened material is decreased. Ductility is the extent to which a material can undergo plastic deformation, that is, it is how much a material can be plastically deformed before fracture. A cold-worked material is, in effect, a normal (brittle) material that has already been extended through part of its allowed plastic deformation. If dislocation motion and plastic deformation have been hindered enough by dislocation accumulation, and stretching of electronic bonds and elastic deformation have reached their limit, a third mode of deformation occurs: fracture.

Heat treating (or heat treatment) is a group of industrial, thermal and metalworking processes used to alter and modify the physical and mechanical properties of fasteners. Heat treatment involves the use of heating or chilling, normally to extreme temperatures, to achieve the desired result such as hardening or softening of fasteners. Heat treatment techniques include annealing, case hardening, precipitation strengthening, tempering, carburizing, normalizing and quenching. A hard, brittle crystalline structure or extremely brittle zone may occur during heat treating process. It may be too brittle to be useful for most applications. Without toughness, the rupture and fracture of fasteners by embrittlement shall be found in use.

Adsorption embrittlement is the embrittlement caused by wetting that is similar to hydrogen absorption to cause embrittlement of materials to failure perform in brittle fractography. Stress corrosion cracking (SCC) relies on both a corrosive environment and the presence of tensile (not compressive) stress. For example, Sulfide stress cracking of fasteners is a typical stress corrosion phenomenon of the embrittlement caused by absorption of hydrogen sulfide corrosive environment and the presence of tensile.

Most embrittlement mechanisms can cause fracture transgranularly or intergranularly. There exists the same embrittlement mechanisms on fasteners. For embrittlement of fasteners, only certain combinations of fastener materials, stresses, and temperatures are susceptible. This is contrasted to stress-corrosion cracking where virtually any metal can be susceptible given the correct environment.

Except for work hardening, The rupture and fracture of fasteners by embrittlement shall be focused on the three common embrittlement topics, such as Temper Embrittlement (TE), Hydrogen embrittlement (HE) and Stress corrosion cracking (SCC) of fasteners. Temper Embrittlement (TE) and Hydrogen embrittlement (HE) shall have to be examined and tested for susceptibility after the fasteners were manufactured and before in use and application. Stress corrosion cracking (SCC) of fasteners should be found often when fasteners were in use for a period of duration in certain environment atmosphere/condition and stressed situation.

2. Temper Embrittlement

Temper Embrittlement (TE) occurs in steel alloys of fasteners that contain certain tramp elements i.e. antimony, arsenic, phosphorus, and tin. If these alloys of fasteners are held between a critical temperature range for a period of time, tramp elements can segregate to grain boundaries. There is a time factor to TE; as more impurities build up on the grain boundaries the alloy of fasteners becomes more brittle in nature. The susceptible temperature range and hold times will vary between alloys, and each steel grade will have its own range of temperatures to avoid.

Temper embrittlement can occur at any time the fastener alloy passes through the embrittlement temperature range for an extended period of time, e.g. during tempering and/or during slow cooling. To reduce temper embrittlement, make sure to temper outside the critical temperature range. Also, make sure to fast cool the alloy through its embrittlement temperature. This will assure the tramp elements do not have time or energy to segregate to grain boundaries.

The microstructural and property changes accompanying the tempering of quenched low-alloy steel fasteners have been examined and correlated with the tempered martensite embrittlement (TME) phenomenon.

In some steels with low alloy content, tempering in the range of 260 and 340 °C (500 and 644 °F) causes a decrease in ductility and an increase in brittleness, and is referred to as the "tempered martensite embrittlement" (TME) range. The embrittlement was found to be concurrent with the interlath precipitation of cementite during tempering and the consequent mechanical instability of interlath films of retained austenite during subsequent loading. (see **Figure 1**)

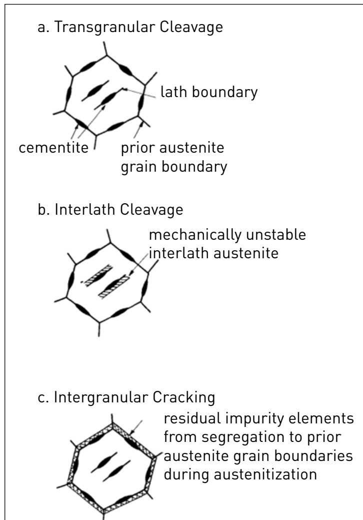

Figure 1. Schematic diagrams of mechanisms of tempered martensite embrittlement

Reference:
Page.1051, Volume 9A, Metallurgical Transactions A, August 1978

At about 600 °C (1,112 °F), the steel fastener may experience another stage of embrittlement during heat treatment process which occurs if the steel is held within the TE temperature range for too long. When heating above this temperature, the steel fastener will usually not be held for any amount of time, and quickly cooled to avoid temper embrittlement.

3. Rupture and Fracture of Fasteners by Hydrogen Embrittlement

Hydrogen embrittlement is a metal fastener's loss of ductility and reduction of load bearing capability due to the absorption of hydrogen atoms or molecules by the metal. The result of hydrogen embrittlement is that components crack and fracture at stresses less than the yield strength of the metal fastener.

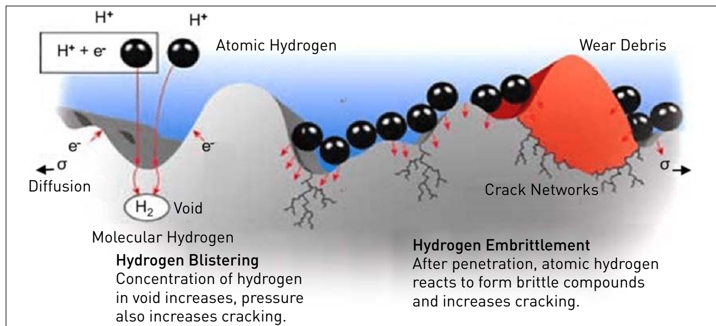

Figure 2. Schematic view of hydrogen embrittlement process

Reference:
www.researchgate.net/figure/Schematic-view-of-hydrogen-embrittlement-process-1_fig1_305926666

It will be few probability for absorption of hydrogen of fasteners in normal air atmosphere because hydrogen is the lightest element, and atomic or molecular hydrogen exists only about 500 ppb of volume percentage or 36 ppb of weight percentage in normal air atmosphere on earth surface.

Fastener manufacturing processes for which there is a possibility of absorption of hydrogen include acid pickling and electroplating. Hydrogen is present in acid pickling baths before fastener electroplating, galvanizing, or surface cleaning.

During electroplating process, hydrogen is produced at the surface of the fastener being coated. Acid pickling is used to remove oxide scale and rust from the surface of steel fasteners and electroplating is commonly used to deposit zinc on steel nuts, bolts, screws and other fasteners for galvanic corrosion protection of the steel fasteners. Other electroplated coatings are used for different applications.

Hydrogen absorption can also occur when a component is in service if the steel fastener is exposed to acids, hydrogen rich environment, or hydride chemicals if hydrogen absorption of the steel fastener occurs. Schematic view of hydrogen embrittlement process is shown in **Figure 2**.

The embrittlement process is followed by absorption of hydrogen by metal material of fasteners. At room temperature or within a specified temperature range, hydrogen atoms can be absorbed by carbon steel alloys or metal alloys of fasteners. The absorbed hydrogen may be present either as atomic or molecular form. Given enough time, the hydrogen diffuses to the metal grain boundaries and forms bubbles at the metal grain boundaries. These bubbles exert pressure on the metal grains. The pressure can increase to levels where the metal has reduced ductility and strength. (See **Figure 3**)

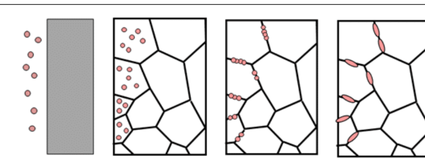

Figure 3. Absorption of hydrogen, hydrogen diffusion and forming bubbles at the metal grain boundaries

Reference:
https://www.imetllc.com/training-article/hydrogen-embrittlement-steel/

Hydrogen embrittlement (HE) also known as hydrogen assisted cracking (HAC) and hydrogen-induced cracking (HIC), practically describes the embrittling of metal after being exposed to hydrogen. It is a complex process that is not completely understood because of the variety and complexity of mechanisms that can lead to embrittlement. Mechanisms that have been proposed to explain embrittlement include the formation of brittle hydrides, the creation of voids that can lead to bubbles and pressure build-up within a material and enhanced decohesion or localised plasticity that assist in the propagation of cracks.

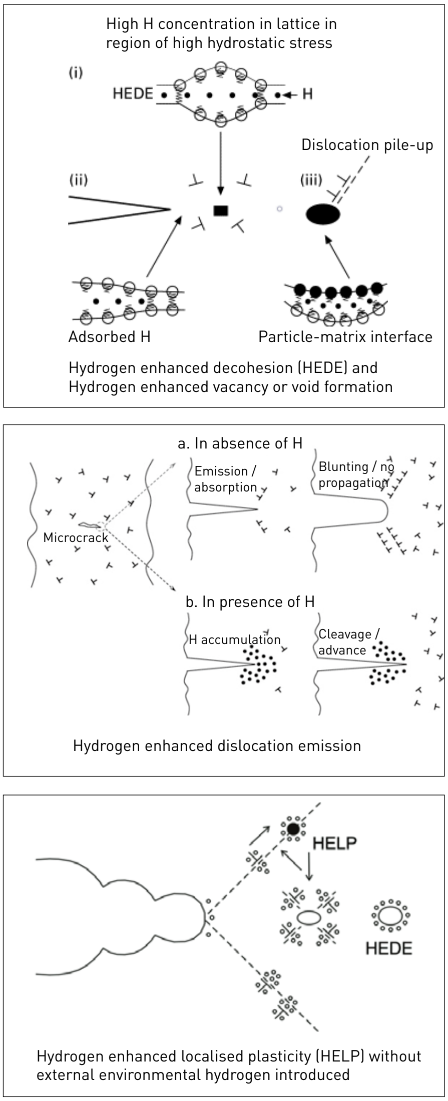

Figure 4. Variety of hydrogen embrittlement mechanisms

Reference:
https://www.sciencedirect.com/topics/engineering/decohesion
https://www.researchgate.net/figure/Schematic-illustration-of-three-hydrogen-embrittlement-mechanisms-Hydrogen-Enhanced_fig1_325086541

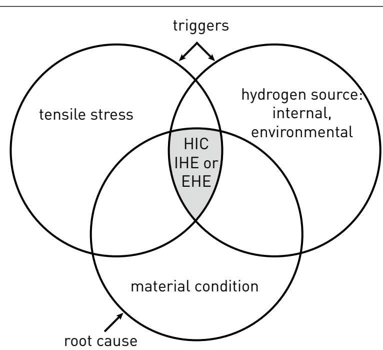

Figure 5. Two categories of failure induced by hydrogen-induced cracking (HIC).

Reference:
https://royalsocietypublishing.org/doi/full/10.1098/rsta.2016.0407

There are a variety of embrittlement mechanisms that have been proposed:

(1) Internal pressure:

Adsorbed hydrogen species recombine to form hydrogen molecules, creating pressure from within the metal. This pressure can increase to levels where the metal has reduced ductility, toughness, and tensile strength, up to the point where it cracks open (hydrogen-induced cracking, or HIC).

(2) Metal hydride formation:

The formation of brittle hydrides with the parent material allows cracks to propagate in a brittle fashion.

(3) Phase transformations:

Phase transformations occur for some materials when hydrogen is present.

(4) Hydrogen enhanced decohesion:

Hydrogen enhanced decohesion (HEDE) where the strength of the atomic bonds of the parent material are reduced. (see **Figure 4**)

(5) Hydrogen enhanced localised plasticity:

Hydrogen enhanced localised plasticity (HELP) is the process where the generation and movement of dislocations is enhanced and results in localised deformation such as at the tip of a crack increasing the propagation of the crack with less deformation in surrounding material giving a brittle appearance to the fracture. Experiments have shown that stationary dislocations begin to move when molecular hydrogen is dissociated and absorbed into pre-strained material. (see **Figure 4**)

(6) Hydrogen enhanced vacancy formation:

Vacancy production can be increased in the presence of hydrogen but since vacancies cannot be readily eliminated this proposal is inconsistent with observations that the removal of hydrogen reduces the embrittlement. (see **Figure 4**)

(7) Hydrogen enhanced dislocation emission:

Hydrogen enhanced dislocation emission proposes that hydrogen is adsorbed onto to the surface and allows dislocations to be generated at lower stress levels thus increasing the level of localised plasticity at the tip of a crack allowing it to propagate more freely. (see **Figure 4**)

There are many sources of Hydrogen Embrittlement, however they can be divided into two categories based on how the hydrogen is introduced into the metal; Internal Hydrogen Embrittlement (IHE) and Environmental Hydrogen Embrittlement (EHE) or so called External Hydrogen Embrittlement (EHE) . The three conditions must be met in sufficient and overlapping quantities for hydrogen-induced cracking (HIC) failure to occur. Stress and hydrogen are triggers, whereas material susceptibility is the fundamental requirement for HE to occur and is therefore associated with the root cause. (See **Figure 5**)

The first category is from the pre-existing hydrogen already present within the metal fastener from creation. Examples of Internal Hydrogen Embrittlement include processes such as casting, carbonizing, surface cleaning, pickling, electroplating, electrochemical machining, welding, roll forming, and heat treatments. Hydrogen formed on the surface of the steel by a cathodic corrosion reaction can diffuse into the steel fastener material, causing embrittlement, and, if the region is subject to tensile stress, cracking can occur. (**Figure 6**)

Internal Hydrogen Embrittlement (IHE) can be prevented through several methods, all of which are centered on minimizing contact between the metal and hydrogen, particularly during fabrication and the electrolysis of water. Embrittling procedures such as acid pickling should be avoided, as should increased contact with elements such as sulfur and phosphate. The use of proper electroplating solution and procedures can also help to prevent IHE. If the fastener has not yet started to crack or to be stressed in use, hydrogen embrittlement can be reversed by removing the hydrogen source and causing the hydrogen within the fastener to diffuse out through heat treatment. This de-embrittlement process, known as "baking", is used to overcome the weaknesses of methods such as electroplating which introduce hydrogen to the plated fastener, but is not always entirely effective because a sufficient time and temperature must be reached. ASTM F1624 can be used to rapidly identify the minimum baking time (by testing using design of experiments. A relatively low number of samples can be used to pinpoint this value).

In fact, the Standard Test Method for Process Control Verification to Prevent Hydrogen Embrittlement shall be taken as the rating criteria for Internal Hydrogen Embrittlement (IHE) without external hydrogen source or environmental factors to be introduced. It can be taken to a proper way to identify the Hydrogen-induced cracking (HIC) caused by IHE or EHE. It is done in normal ambient air atmosphere often. It will be taken to the basic criteria to identify the baseline of with or without Stress Corrosion Cracking phenomena when the external environmental factor is introduced.

Most analytical methods for hydrogen embrittlement involve evaluating the effects of internal hydrogen from production. ASTM F1940 is the Standard Test Method for Process Control Verification to Prevent Hydrogen Embrittlement in Plated or Coated Fasteners. While the title now explicitly includes the word, fasteners, ASTM F1940 was not originally intended for these purposes. ASTM F1940 is based on the ASTM F1624 method and is similar to ASTM F519 but with different root radius and stress concentration factors. When specimens exhibit a threshold cracking of 75% of the net fracture strength, the plating bath is considered to be 'non-embrittling'.

The second category is hydrogen introduced from the environment. Hydrogen-induced cracking (HIC) failure is hydrogen introduced outside instead of pre-existing hydrogen in fasteners. Examples of Hydrogen Environmental Embrittlement include generic corrosion from exposure to the environment or through misapplication of various protection measures. For example, the combined effects of stress and corrosion can cause special types of failure: Chloride SCC (Stress Corrosion Cracking), Sulphide SCC, Polythionic acid SCC, and so on. EHE pertains to the incursion of hydrogen from external sources like hydrogen molecular rich or hydrogen ion environment. Stress corrosion cracking is an example of EHE. EHE is also an example of stress corrosion cracking.

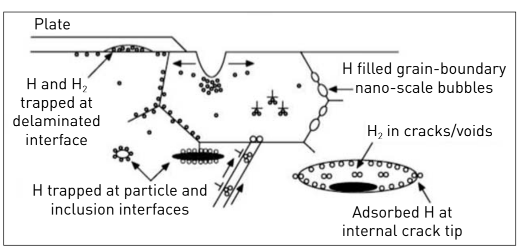

Figure 6. The pre-existing hydrogen is already present and formed within the metal from creation.

Reference: https://www.sciencedirect.com/topics/engineering/lattice-site

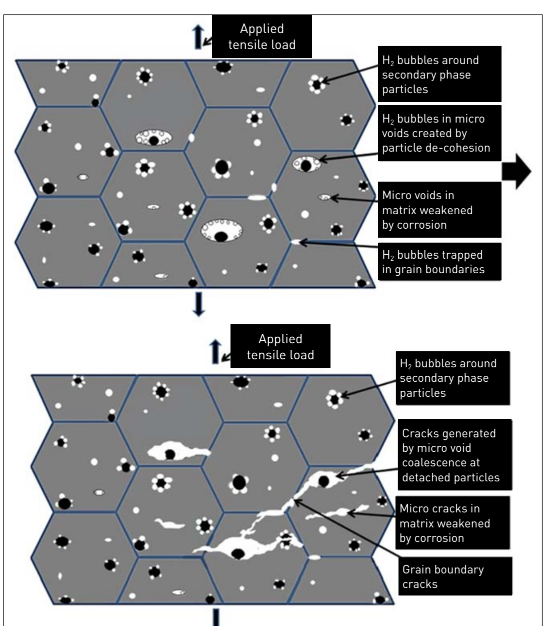

Figure 7. Schematic representation of the mechanism of hydrogen embrittlement that results from H traps at voids, secondary phase particles and grain boundaries.

Reference:
https://www.researchgate.net/figure/Schematic-representation-of-the-mechanism-of-hydrogen-embrittlement-that-results-from-H_fig15_335650001