Hydrogen Embrittlement

by:
Daniel H. Herring
"The Heat Treat Doctor"®, President
The HERRING GROUP, Inc.
P.O. Box 884
Elmhurst, IL 60126-0884 USA
www.heat-treat-doctor.com

Although many of the most severe hydrogen embrittlement problems have occurred in aircraft applications, it should be remembered "that it doesn't have to fly in order to die".

Embrittlement is a phenomenon that causes loss of ductility in a material, thus making it brittle. There are a number of different forms including:

- Environmentally Induced Cracking.
- Stress Corrosion Cracking.
- Hydrogen Embrittlement.
- Corrosion Fatigue.
- Liquid Metal Embrittlement.

Of these, hydrogen embrittlement is responsible for a surprising number of delayed failures and problems with products produced from wire, especially if they undergo secondary processing operations such as plating. The factors (see **Figure 1**) responsible for this type of failure include having a susceptible material, an environment conductive to attack and the presence of stress (internal or applied). Once two of these three factors are present, failure is inevitable.

Hydrogen embrittlement is also known as hydrogen induced cracking or hydrogen attack. Materials that are most vulnerable include high-strength steels, titanium and aluminum alloys and electrolytic tough pitch copper. Hydrogen embrittlement mechanisms (see **Figure 2**) can be aqueous or gaseous and involve the ingress of hydrogen into the metal, reducing its ductility and load bearing capacity. Stress below the yield stress of the susceptible material then causes subsequent cracking and catastrophic brittle failures (see **Figure 3**).

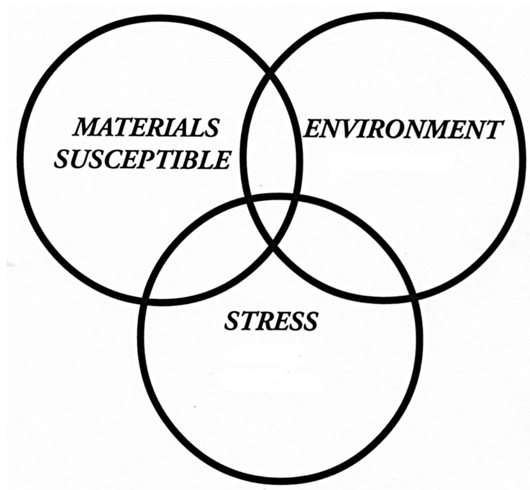

Fig. 1 — Factors contributing to hydrogen embrittlement.

How Hydrogen Gets In

It is generally agreed that hydrogen, in atomic form, will enter and diffuse through a metal surface whether at elevated temperatures or ambient temperature. Once absorbed, dissolved hydrogen may be present either as atomic or molecular hydrogen or in combined molecular form (e.g., methane). Since these molecules are too large to diffuse through the metal, pressure builds at crystallographic defects (dislocations and vacancies) or discontinuities (voids, inclusion/matrix interfaces) causing minute cracks to form. Whether this absorbed hydrogen causes cracking or not is a complex

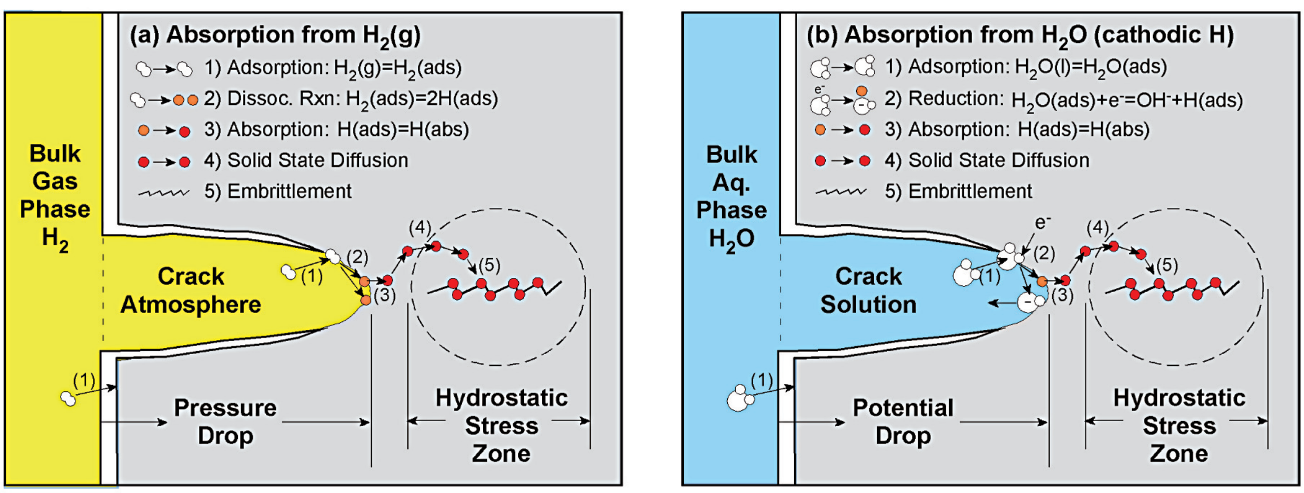

Fig. 2 — Hydrogen embrittlement mechanisms.

interaction of material strength, external stresses and temperature.

Sources of hydrogen include heat treating atmospheres, breakdown of organic lubricants, the steelmaking process (e.g., electric arc melting of damp scrap), the working environment, arc welding (with damp electrodes), dissociation of high pressure hydrogen gas and even grinding (in a wet environment).

Parts that are undergoing electrochemical surface treatments such as etching, pickling, phosphate coating, corrosion removal, paint stripping and electroplating are especially susceptible. Of these, acid cleaning is the most severe, followed by electroplating at high current (these are less efficient and create more hydrogen even though they produce a better plated structure), electrolysis plating and conversion coatings.

Fig. 3 — Hydrogen embrittlement and failure of a hard chromium-plated chain conveyor bolt.

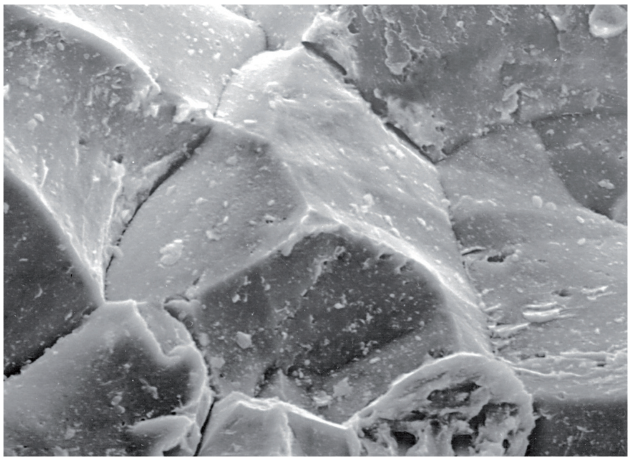

Fig. 4 — Intergranular fracture due to hydrogen embrittlement (photo courtesy of Aston Metallurgical Services Co., Inc.).

Nature & Effect of Hydrogen Attack

Although the precise mechanism(s) is the subject of active investigation, the reality is that components fail due to this phenomenon. It is generally believed that all steels above 30 HRC are vulnerable, as are materials such as copper, whether tough pitch or oxygen-free, titanium and titanium alloys, nickel and nickel alloys and the like. Examples of hydrogen damage and ways to avoid it include the following.

- ***Problem:*** Internal cracking or blistering.
  Solutions: Use of steel with low levels of impurities (i.e., sulfur and phosphorus); modifying the environment to reduce hydrogen charging; use of surface coatings and effective inhibitors.
- ***Problem:*** Loss of ductility.
  Solutions: Use of lower strength (hardness) or high resistance alloys; careful selection of materials of construction and plating systems; heat treatment (bakeout) to remove absorbed hydrogen.
- ***Problem:*** High temperature hydrogen attack.
  Solutions: Selection of material (for steels, use of low and high alloy Cr-Mo steels, selected Cu alloys, nonferrous alloys); limit temperature and partial pressure H_2.

Since a metallurgical interaction occurs between atomic hydrogen and the crystallographic structure, the ability of the material to deform or stretch under load is inhibited. Therefore, it becomes "brittle" under stress or load. As a result, the metal will break or fracture at a much lower load or stress than anticipated. It is this lower breaking strength that makes hydrogen embrittlement so detrimental.

In general, as the strength of the steel goes up, so does its susceptibility to hydrogen embrittlement. High-strength steel, such as quenched and tempered steels or precipitation-hardened steels, is particularly susceptible. Hydrogen embrittlement is considered the Achilles heel of high strength ferrous steels and alloys.

And nonferrous materials are not immune to attack. Tough-pitch coppers and even oxygen-free coppers are subject to a loss of (tensile) ductility when exposed to reducing atmospheres. Bright annealing in hydrogen bearing furnace atmospheres, oxy-acetylene torch brazing and furnace brazing are typical processes that can create hydrogen embrittlement of these materials.

The attack in these copper alloys involves the diffusion of atomic hydrogen into the copper and subsequent reduction of cuprous oxide (Cu_2O) to produce water vapor and pure copper. An embrittled copper often can be identified by a characteristic surface blistering resulting from expansion of water vapor in voids near the surface. Purchasing oxygen-free copper is no guarantee against the occurrence of hydrogen embrittlement, but the degree of embrittlement will depend on the amount of oxygen present.

For example, CDA 101 (oxygen-free electronic) allows up to 5 ppm oxygen while CDA 102 (OFHC) permits up to 10 ppm. A simple bend test is often used to detect the presence of hydrogen embrittlement. Metallographic techniques (**Figure 4**) can also be used to look at the near surface and for the presence of voids at grain boundaries.

How Hydrogen Gets Out?

Hydrogen absorption need not be a permanent condition. If cracking does not occur and the environmental conditions are changed so that no hydrogen is generated on the surface of the metal, the hydrogen can re-diffuse out of the steel, and ductility is restored. Performing an embrittlement relief, or hydrogen bake out cycle (the term "bake-out" involves both diffusion within the metal and outgassing) is a powerful method in eliminating hydrogen before damage can occur.

Some of the key variables include temperature, time at temperature, and concentration gradient (atom movement).

For example, electroplating provides a source of hydrogen during the cleaning and pickling cycles, but by far the most significant source is cathodic inefficiency. A simple hydrogen bake out cycle can be performed to reduce the risk of hydrogen damage (**Table 1**).

Caution: over-tempering or softening of the steel can occur, especially on a carburized, or induction hardened part.

Table 1. Hydrogen Bake-Out Requirements for High Strength Parts.

Tensile Strength		Hardness (HRC)	Time (hrs) Post Plate Bake Out at 375º- 430ºF (190º - 220ºC)
MPa	ksi		
1700 – 1800	247 – 261	49 – 51	22+
1600 – 1700	232 – 247	47 - 49	20+
1500 – 1600	218 – 232	45 - 47	18+
1400 – 1500	203 – 218	43 - 45	16+
1300 – 1400	189 – 203	39 – 43	14+
1200 – 1300	174 – 189	36 – 39	12+
1100 – 1200	160 – 174	33 – 36	10+
1000 – 1100	145 -160	31 – 33	8+

Note: Per *ASTM B 850-98 (2009)*, Standard Guide for Post-Coating Treatments of Steel for Reducing the Risk of Hydrogen Embrittlement.

Factors that Influence Hydrogen Embrittlement on Parts

The severity and mode of the hydrogen damage depends on:

- Source of hydrogen—external (gaseous)/internal (dissolved).
- Exposure time.
- Temperature and pressure.
- Presence of solutions or solvents that may undergo some reaction with metals (e.g., acidic solutions).
- Type of alloy and its production method.
- Amount of discontinuities in the metal.
- Treatment of exposed surfaces (barrier layers, e.g., oxide layers as hydrogen permeation barriers on metals).
- Final treatment of the metal surface (e.g., galvanic nickel plating).
- Method of heat treatment.
- Level of residual and applied stresses.

Low Hydrogen Concentrations Can Also Be Problematic

Of concern today is embrittlement from very small quantities of hydrogen where traditional loss-of-ductility bend tests cannot detect the condition. This atomic level embrittlement manifests itself at levels as low as 10 ppm of hydrogen (in certain plating applications it has been reported that 1 ppm of hydrogen is problematic).

Although difficult to comprehend, numerous documented cases of embrittlement failures with hydrogen levels this low are known. This type of embrittlement occurs when hydrogen is concentrated or absorbed in certain areas of metallurgical instability.

This type of concentrating action occurs as a result of either residual or applied stress, which tends to "sweep" through the atomic structure, moving the infiltrated hydrogen atoms along with it. These concentrated areas of atomic hydrogen can then coalesce into molecular-type hydrogen, resulting in the formation of highly localized partial pressures of the actual gas.

What Type of Parts Are Susceptible?

Although almost any type of part is subject to hydrogen embrittlement, certain components such as fasteners and nuclear components are most susceptible.

Ways to Avoid Hydrogen Embrittlement

Steps that can be taken to avoid hydrogen embrittlement include reducing hydrogen exposure and susceptibility, baking after plating (mandatory and as soon as practical) and using test methods to determine if a material is suspect.

Other options that could help in avoiding hydrogen embrittlement include the use of lower strength steels (not always viable), the avoidance of acid cleaning, the utilization of low hydrogen plating techniques and the reduction of residual and applied stress.

Where to Go For Help?

A good, but relatively unknown source for information about the effects of hydrogen, is the **NACE International**, **The Corrosion Society** (*www.nace.org*). Also, various **ASTM** specifications (*www.astm.org*) can also help, including *ASTM B850-98, 2009* (Standard Guide for Post-Coating Treatments of Steel for Reducing the Risk of Hydrogen Embrittlement); *ASTM F1113-97* (The Barnacle Electrode Method to Determine Diffusible Hydrogen in Steels); *ASTM F519-08* (Standard Test Method for Mechanical Hydrogen Embrittlement Evaluation of Plating/Coating Processes and Service Environments); and *ASTM F1624-09* (Standard Test Method for Measurement of Hydrogen Embrittlement Threshold by the Incremental Step Loading Technique).

The Bottom Line

Although many of the most severe problems associated with hydrogen embrittlement have occurred with aircraft/aerospace parts, a simple motto to remember is that the part doesn't have to "fly" in order to "die".

The insidious nature of hydrogen embrittlement continues to cause product failures during processing and during service. These failures are often catastrophic, leading to injury or damage to adjacent structures, and are difficult to detect after the fact. For this reason, hydrogen damage can and must be avoided.

For additional information on dealing with hydrogen embrittlement, visit the website listed below.
www.heat-treat-doctor.com **WFTI**

References:

- *Herring, D. H., and Richard D. Sisson, Jr., The Heat Treatment of Fasteners – Embrittlement Issues, Fastener Technology International, December 2008.*
- *Herring, D. H., The Embrittlement Phenomena in Hardened & Tempered Steels, Industrial Heating, October 2006.*
- *Herring, D. H., A Heat Treaters Guide to Hydrogen Embrittlement, Industrial Heating, October 2004.*