Embrittlement

Hydrogen Embrittlement

Hydrogen embrittlement is generally associated with high-strength fasteners made of carbon and alloy steels. However, it is worth noting that even precipitate hardened stainless steels, titanium, and aluminum alloys can be vulnerable. Hydrogen embrittled fasteners or parts under stress can fail suddenly without any warning. There are many different theories on the exact cause. The following is our comprehension of the subject.

Hydrogen is the most common element in the world and many acidic and oxidation reactions with steel will liberate hydrogen in various amounts depending on the specific chemical reaction.

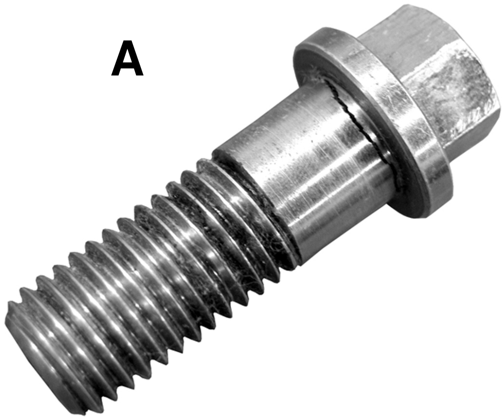
Hydrogen embrittlement can occur whenever atomic or protonic hydrogen is produced from a reaction, e.g. acid pickling can react iron and hydrochloric acid to diffuse hydrogen in iron. During acid pickling hydrogen can be diffused into the iron. Electroplating is another process to introduce hydrogen into a metal in both the acid pickle and the plating processes. Another example of hydrogen production is from high pressure steam. The table on the right shows the simplified chemical reactions of the processes mentioned herein.

Metallic Reactivity in the Presence of Acids	
Hydrochloric Acid	$Fe_{(s)} + HCl_{(aq)} \rightarrow Fe_{(s)} + H + \frac{1}{2}Cl_{2(g)} \rightarrow FeH_{(s)}$
Electroplating	$M + H_2O + e^- \rightarrow M + H + OH^- \rightarrow MH + OH^-$ $M + H_3O^+ \rightarrow M + H^+ + H_2O \rightarrow MH^+ + H_2O$
High-Pressure Steam	$4Fe_{(s)} + 6H_2O_{(g)} \rightarrow 2Fe_2HO_3 + 5H_{2(g)}$
Key:	
Element	**Symbol**
Iron	Fe
Hydroden	H
Water	H_2O
Hydrochloric Acid	HCl
Generic Metal	M
Generic Acid	H_3O^+
Electron	e^-
Note: the end product always has hydrogen embedded in a metal	

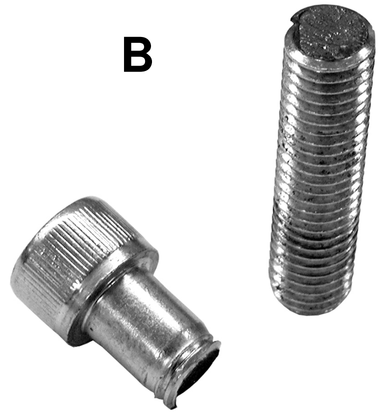
Internal hydrogen embrittlement is the more common form of hydrogen embrittlement and can occur any time atomic hydrogen is absorbed into the fastener from any chemical process before exposure to an externally applied stress.

Frequently, hydrogen is introduced to the fastener during the electroplating process. In these cases, the hydrogen is absorbed into the fastener during the acid cleaning or **descaling** process and is then trapped in the part by the plating. A subsequent baking process is typically employed to remove or displace the trapped hydrogen. Even proper baking is no guarantee of freedom from hydrogen. When tension is applied to the fastener, the hydrogen tends to migrate to points of high stress concentration (under the head of the fastener, first engaged thread, etc.). The pressure created by the hydrogen creates and/or extends a preexisting crack which grows under subsequent stress cycles until the bolt breaks.

A



B



Although the most common hydrogen embrittlement failures are directly underneath the head of the fastener (A), they can also occur elsewhere given proper circumstances (B). Lab analysis is always necessary to determine the proper cause of a failure.

Unfortunately this is only one of several models of hydrogen embrittlement. As mentioned previously, any chemical process that introduces hydrogen into the material can lead to embrittlement. Other sources of hydrogen can include the melting of steel, processing parts, or even welding. Regardless of the means of transmission, all internal hydrogen embrittlement is the result of hydrogen absorption by the base metal prior to the application of stress.

Environmental hydrogen embrittlement (EHE) is another form of hydrogen embrittlement. This is generally caused by hydrogen introduced into the steel from the environment after being placed in service. In this case, the hydrogen can come from a number of external sources or as by-product of general corrosion, or a by-product of a common reaction.

Stress corrosion (a form of environmental hydrogen embrittlement) represents a particular condition where cracks are induced and propagated under combined effects of stress and corrosion environments. It is the least understood corrosion related phenomenon, but by far the most dangerous. Under the right conditions, any metal is susceptible to this type of corrosive attack. The initial corrosion may occur at a point of high stress causing the formation of a microscopic crack, which can be either intergranular or transgranular. Continued exposure to the corrosion environment will propagate the crack, resulting in serious and possibly catastrophic failure.

Stress corrosion, along with other material failure modes such as stress embrittlement, environmental hydrogen embrittlement, and hydrogen assisted stress corrosion differ from internal hydrogen embrittlement because they are all related to the service environment. These failures occur after installation due to hydrogen being introduced by a chemical reaction induced by the service environment.

Methods for Fighting Hydrogen Embrittlement

Below are a few methods used to fight hydrogen embrittlement:

Hardness is a major contributor to hydrogen embrittlement. Harder, stronger materials are more susceptible to failure than weaker, softer ones. In general, if the hardness of the fastener is less than 35

HRC, there will probably be little difficulty with hydrogen embrittlement. However, if the fastener has hardness above 40 HRC, problems are more likely to occur.

Hydrogen concentration is another factor that contributes to hydrogen embrittlement. Coating processes such electroplating can introduce hydrogen during the acid cleaning stage. During this stage, the material to be plated is immersed in an acidic solution. Higher acid concentrations and long exposure times will increase the hydrogen concentration in the fastener material, thus increasing the likelihood of hydrogen embrittlement.

Using a coating process that does not introduce hydrogen into the material (particularly those that do not utilize acids for cleaning) will help avoid this problem. A number of dip-spin coatings are considered hydrogen embrittlement "free" because they use mechanical processes (abrasive blasting) for descaling. Additionally, some of these coatings offer higher corrosion resistance and therefore less vulnerability to EHE.

Coating porosity also has an impact on hydrogen concentration. Electroplated coatings are dense enough to "trap" or seal hydrogen in the base material. Once the hydrogen is sealed in the fastener, it is more likely to produce an embrittlement failure. Mechanical coatings are more porous (less dense). Therefore, any hydrogen in the base material of a mechanically coated fastener will have a better opportunity to escape without causing an embrittlement failure.

If electroplating is still desired, ensure that the plater uses the proper procedures and bakes the fasteners correctly based on the hardness of the fastener.

ASTM F1941 has a hydrogen embrittlement relief requirement for coated fasteners made from steel heat treated to a hardness of HRC 40 or above, case hardened fasteners, and fasteners with captive washers (SEM screws) made from hardened steel. The exact time and temperature of the bake is not specified, but times between 2 and 24 hours at temperatures between 350 and 450°F are listed as suitable depending on type, size of fastener, geometry and other variables.

Environment ought to be one of the major concerns of bolted joint design. Proper selection of the fastener material for the service environment can reduce the risk of embrittlement. The potential for hydrogen embrittlement cracking (even for fasteners below HRC 35) is accelerated if the fastener is acting as the cathode in a galvanic couple. Caustic or sour environments may require much lower hardness levels to lower the susceptibility to hydrogen embrittlement.

Temper Embrittlement

Temper Embrittlement (TE) occurs in some alloys that contain certain tramp elements i.e. antimony, arsenic, phosphorus, and tin. If these alloys 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 becomes more brittle in nature. The susceptible temperature range and hold times will vary between alloys, but in general the embrittlement temperatures can range from 660 °F to 1060 °F. Again, please note, each metal will have its own range of temperatures to avoid.

Temper embrittlement can occur at any time the alloy passes through the embrittlement temperature range for an extended period of time, e.g. during tempering and/or during slow cooling. Large pieces of alloy are more susceptible to TE due to the interior not being able to cool as quickly. See *Heat Treatment* for more explanation on the topic of uniform 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.

Temper embrittlement is reversible! If parts are suspected of being tempered or slow cooled between the embrittlement temperature range the parts can be re-tempered (at a temperature outside the range). By re-tempering, TE can be drastically (if not completely) reduced.