Hydrogen Induced Corrosion

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Introduction

One typically thinks of corrosion as electrochemical reactions that destroy metal surfaces through oxidation. Hydrogen corrosion works through mechanisms in which metals are weakened internally. Due to its relatively small size, hydrogen is able to penetrate into metals and affect properties such as strength and ductility. This occurs through embrittlement, blistering, precipitation, hydride formation, and reaction with embedded carbon. This paper describes the sources of hydrogen corrosion, the details the mechanisms of corrosion and methods used prevention.

Sources of Hydrogen Corrosion

Hydrogen damage of metals occurs when hydrogen is absorbed in metal and thus weakens the load-carrying capacity of the metal. Metals absorb hydrogen when in an environment that contains or generates hydrogen. This can be during the production, processing, and/or the service of the metal.

Hydrogen can be absorbed during the production of forged steel. In steelmaking, hydrogen comes from the moisture in the atmosphere and from additives used during processing. It dissolves more in the high-temperature FCC austenite state (γ-iron) than in the lower temperature BCC ferrite state (α-iron). Therefore, when hydrogen is absorbed in the γ-iron state and subsequently cooled, the individual hydrogen atoms precipitate in the α-iron at inclusions or micropores. The pressure of the hydrogen gas creates what are called "flakes" in the metal, causing embrittlement. Similar damage can occur when steel is welded in an environment that contains hydrogen, which can be introduced through atmospheric or surface contamination. As the welded metal containing hydrogen cools, it becomes super-saturated, and hydrogen diffuses into the surrounding metal heated during the process. As a result, the area around the weld becomes embrittled by subsequent corrosion.

Hydrogen can also be absorbed by metal during aqueous corrosion or cathodic charging. When corrosion occurs in a low-pH solution, some of the reduced hydrogen does not form H_2, but instead, diffuses into the metal as atomic hydrogen. This can happen during pickling and electroplating of metal. Substances such as arsenic, antimony, sulfur, selenium, tellurium, and cyanide ions prevent the hydrogen atoms from forming H_2, and are called cathodic poisons. Cathodic poisons facilitate contamination by keeping hydrogen in atomic form, in which hydrogen more readily diffuses into the metal. Environments containing hydrogen sulfide, which contains both hydrogen and a cathodic poison (i.e. sulfur), are especially dangerous for alloys and metals. Hydrogen sulfide is often encountered in the petroleum industry—during the drilling and completion of oil and gas wells, and during the storage and piping of petroleum products containing hydrogen sulfide.

If steel is in a hydrogen environment of high temperature and pressure, hydrogen attack can occur. Hydrogen is absorbed into the steel, and although the steel may appear fine for a while, it will suddenly lose its strength and ductility. The hydrogen reacts with the carbides inside the steel. This delayed attack is encountered in petrochemical plants, where hydrogen and hydrocarbon streams are at high temperatures and pressures.

Hydrogen can react directly with the metal to form hydrides. This can occur in metals such as titanium, zirconium, uranium, and their alloys. The formation of hydrides can severely weaken these metals. For example, zirconium hydride is so brittle and weak that it can be crushed into powder. Hydrogen can be absorbed during melting, welding, or pickling; it can also be absorbed from water vapor and hydrocarbons.

Aside from hydrogen attack, which occurs at high temperatures, the majority of corrosion occurs at ambient temperature. This is because at high temperatures, the mobility of hydrogen is great enough that there is little accumulation of it at any one location in the lattice. Once ambient conditions are met, solubility decreases and causes pockets of hydrogen to form. This compounded with the decrease in mobility traps the hydrogen within the metal lattice. The process by which hydrogen accumulation leads to corrosion is the topic of the next section

Principles of Hydrogen-Assisted Corrosion

Hydrogen Embrittlement

The presence of hydrogen in steel reduces the tensile ductility and causes premature failure under static loads that depend on the stress and time. This phenomenon is known as hydrogen embrittlement. Although many mechanisms of hydrogen embrittlement have been proposed, all can be classified according to one of three theories: the planar pressure theory, the reduced surface energy theory, and the decohesion theory. All of these theories are explored below. The basic processes involved in hydrogen embrittlement are illustrated in Figure 1.
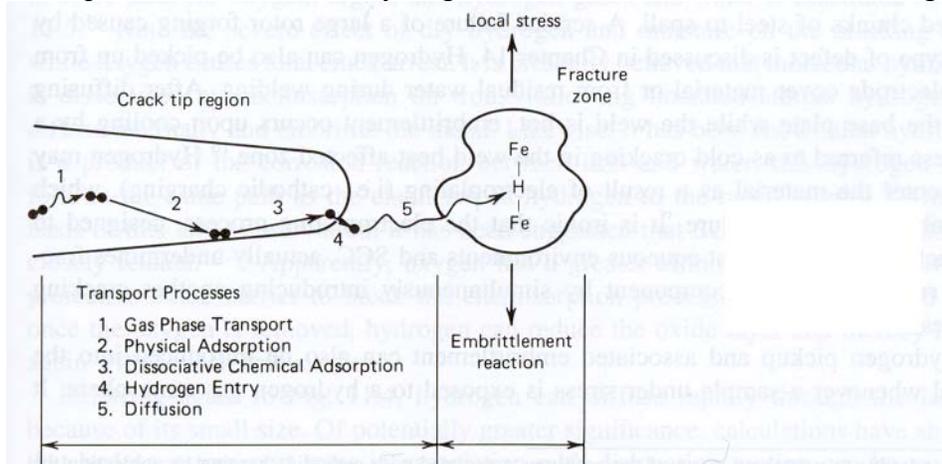

FIGURE 1. **Various processes involved in the hydrogen embrittlement of ferrous alloys.**

Steel can be embrittled by a very small amount of hydrogen, on the level of a few parts per million. This hydrogen may come from some of the many sources described above. Unlike other modes of environmentally-assisted cracking, such as stress corrosion cracking, cracks caused by hydrogen embrittlement usually do not branch. Cracks can develop by both transgranular and intergranular paths. The path of crack growth in hydrogen embrittled steels is a function of the stress intensity factor, K (MPa√m). Examples of crack growth due to hydrogen embrittlement are schematically shown in Figure 2 below.
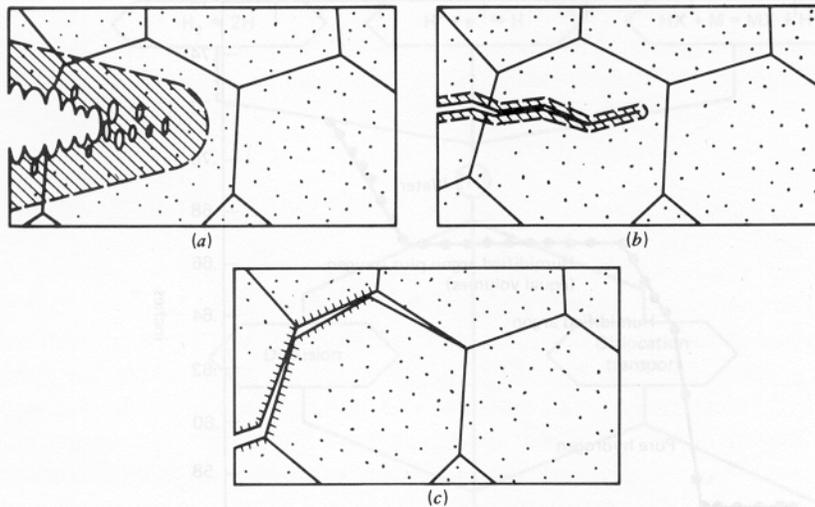
FIGURE 2. Schematic representation of different hydrogen-induced fracture paths as a function of stress level. (a) High K level generates microvoid coalescence; (b) intermediate K level generates transgranular fracture by a quasicleavage mechanism; (c) low K level leads to intergranular fracture path.

Failure caused by hydrogen embrittlement is usually accompanied by very little plastic deformation. The fracture mode is usually brittle cleavage or quasi-cleavage fracture. In general, materials become more vulnerable to hydrogen embrittlement with increased strength. This behavior is supported by the decohesion theory of embrittlement. Decohesion theory states that dissolved hydrogen migrates into a triaxially stressed region and embrittles the lattice by lowering the cohesive strength between metal atoms. This type of fracture is shown in Figure 2a above. During stress cracking, in front of a crack tip there is a localized region where stress is a maximum. On the crack surface, hydrogen gas will physisorb near the crack tip. The hydrogen gas then breaks into atomic hydrogen via chemiadsorption, and the atomic hydrogen will preferentially migrate towards the region of localized maximum stress in front of the crack tip. At this point, the hydrogen is suspected to weaken the metal bonds and may coalesce to form microvoids leading the crack tip. Both possibilities reduce the energy necessary to form brittle crack surfaces. This mechanism is very similar to the reduced surface energy theory, which simply states that the absorption of hydrogen decreases the surface free energy of the metal, enhancing propagation of the crack tip. This theory may explain the crack propagation of high-strength steels in low-pressure hydrogen environments.

For a given hydrogen content, the tendency to embrittle increases with decreased strain rate, and the embrittlement is more prevalent at room temperature. Cracking due to hydrogen embrittlement decreases with increasing temperature, and disappears almost entirely in steels above 200ºC. At high temperatures, hydrogen can be driven out of solid solution given a sufficient period of time. For steels that are charged with a high hydrogen content during solidification, planar pressure theory is held to be a valid mechanism. When steel saturated with hydrogen at elevated temperature is cooled, gaseous hydrogen will precipitate in microvoids. Extremely high-pressure hydrogen can develop in these microvoids. This mechanism appears valid for hydrogen-charged steels, but does not seem valid for steel in low-pressure hydrogen environments. In low-pressure hydrogen environments, it is thermodynamically unfavorable for an external low gas pressure to produce a high gas pressure within a solid. This theory is also used to explain hydrogen induced blistering, which will be discussed below.

Hydrogen Induced Blistering

When hydrogen is absorbed into metal and diffuses inward, it can precipitate as molecular hydrogen, at laminations, or inclusion/matrix interfaces. Each form can build up enough pressure to produce internal cracks. If these cracks are just below the surface, the hydrogen gas pressure in the cracks can lift up and bulge out the exterior layer of the metal so that it resembles a blister. The equilibrium pressure of the molecular hydrogen in the void, which is in contact with the atomic hydrogen in the surrounding metal, is great enough to rupture any metal or alloy. Thus hydrogen induced blistering can be seen as a special case of the plane pressure mechanism of hydrogen embrittlement, where high pressure hydrogen forms in microvoids near the material's surface. Hydrogen induced blistering is most prevalent in low-strength alloys, and is observed in metals that have been exposed to hydrogen-charging conditions.

Precipitation of Internal Hydrogen

The process of refining steels often introduces a hydrogen content of 5-8 parts per million. However, the room temperature solubility of hydrogen in steel is less than 0.1 parts per million. This disturbance from equilibrium causes hydrogen to precipitate in the diatomic form. Hydrogen usually precipitates at previously established inclusions, and the pressure from the precipitation causes the enlargement (or formation) of hairline cracks. Such internal cracks lead to an embrittlement of the steel.

Hydrogen is typically introduced into the steel from excess atmospheric moisture, or contaminants that are already present. At temperatures above 200ºC, most of the hydrogen can escape from the steel and thus the incidence of precipitation flaking is much lower. Flake formation is most favorable at temperatures below 200ºC.

Internal hydrogen damage is also encountered quite frequently in parts that have been welded. Hydrogen is introduced from sources that include the surrounding atmosphere, surface contaminants, and the welding rod itself. Hydrogen embrittlement typically occurs in the metal below the weld root, called the heat-affected zone (HAZ). This form of damage leads to reduced ductility and strength. The fracture surface reveals shiny spots that are referred to as "fish eyes."

Both flakes and fish eyes can be prevented by extended annealing in low hydrogen conditions. This allows the trapped hydrogen to escape from the metal matrix. In the case of welding, this is often not economically feasible. Proper sample preparation to remove contaminants, plus the use of clean inert gases, can lower the risk of internal hydrogen damage. Additionally, hydrogen assisted cracking can be avoided by reducing stress levels in the metal.

Hydrogen Attack

Hydrogen attack can occur in steel that has been subjected to a high-temperature high-pressure hydrogen environment. The term "attack" is used because affected systems typically do not exhibit any signs of weakening before failure occurs at significantly below the yield stress. Unlike hydrogen embrittlement, hydrogen attack is a high-temperature phenomenon because it depends on high concentrations of absorbed hydrogen.

Carbides react with internal hydrogen to form methane, which precipitates in the grain boundaries. Bubbles may form in the matrix, and there may be decarburization at grain boundaries. These processes become significant at temperatures higher than 200ºC. However, rapid quenching of steel that has previously established equilibrium in a high-pressure high-temperature hydrogen environment may cause rapid precipitation and cracking.

Cracking From Hydride Formation

Metals that are susceptible to hydride formation include titanium, tantalum, zirconium, uranium, and thorium. Hydrogen is absorbed into these metals at high temperatures, with subsequent hydride formation upon cooling. Hydride particles tend to increase the strength of the host metal, while causing a decrease in the ductility. These particles typically exhibit lower density than the surrounding matrix, with a preferred orientation in the host matrix. An applied stress can cause these hydride particles to align.

Prevention of Hydrogen Corrosion

In the pursuit to process metals and alloys that are resistant to hydrogen damage, there are two forms of prevention: minimizing hydrogen content and lowering internal stresses. Embrittlement can be reversed with treatment that effectively rids the metal of hydrogen. However, a majority of the work against hydrogen damage is in prevention. The first approach is to improve processing techniques to prevent trapping hydrogen within the metal. The second approach is to optimize the type of metal according to the conditions that the final product will be subject to in operation. Finally, there are certain harmful practices performed on in-service metals that can be curtailed completely.

In the first case, hydrogen induced cracking (HIC) can effectively be reversed with heat treatment. Hydrogen is not very soluble in α-iron state. However, it is especially soluble in the high-temperature γ-iron state above the transformation temperature, 723ºC. Hydrogen mobility is increased at higher temperatures as well. If steels reach high temperatures and high partial pressures of hydrogen, a great deal of hydrogen can penetrate the metal. If it is quenched to a lower temperature, the hydrogen can "freeze" within the metal, allowing HIC to occur at these accumulation spots. Baking between 100ºC and 650ºC under vacuum for extended periods of time will give hydrogen the mobility to diffuse to the surface. Vacuum conditions create a pressure gradient that drives out any hydrogen on the interior.

It most cases, it is not feasible to treat in-service metals. The alternative is to maintain a low hydrogen content from the point of processing before it is put into service. As mentioned before, high temperatures during processing can lead to severe hydrogen contamination. Slow baking while in the BCC ferrite form is the first step to making a metal resistant to HIC. Heat treatment is also recommended before and after welding. However, lower temperatures are sufficient, at 230ºC for one hour per inch of thickness. The welding rod must have low hydrogen content as well. Keeping weld material in dry places is essential to avoid absorption from water vapor.

Some factors that can be optimized for the service of the steels include temperature range, tensile strength, alloying agents, and inhibitors. A majority of hydrogen damage occurs at ambient temperatures. As mentioned before, mobility increases with temperature, preventing accumulation. However, at the same time, the metal is susceptible to hydrogen attack. This involves reactions between the hydrogen and embedded carbides to form methane or decarburized structures. When operating at these high temperatures, the amount of carbon impurities should be minimized to avoid such effects.

A common mistake is to overcompensate with high strength steels where lower strength will perform just as well. Problems arise at high tensile strengths which encourage HIC. A

simple remedy is to determine the highest strength needed for service and match the metal accordingly, leaving no extra chance for HIC to occur.

Metallic alloying agents can create "traps" for the hydrogen. For instance, the addition of 1.5% Ti to iron can increase the time taken for the diffusion of hydrogen to reach its maximum. This is because the hydrogen accumulates at these "traps" before diffusing onward. These traps also reduce the maximum diffusion rate, because they build up micro-gradients that slow diffusion. Another type of additive is the use of corrosion inhibitors. When added to process fluids, they reduce the general corrosion rate. In turn, they slow the generation of hydrogen ions at the surface, reducing the concentration gradient that drives the hydrogen inward.

Some general practices that aid hydrogen damage can be curtailed. For instance, cathodic protection techniques create a source of hydrogen that can diffuse into the protected metal. Stray currents and galvanic couples can create hydrogen as well. If at all possible, supplementing these techniques with other methods that minimize hydrogen creation can prevent corrosion.

Conclusions

The possibility of hydrogen damage should be considered in the design of mechanical systems. In many situations, hydrogen damage is a result of the processing history of the metal; and not necessarily the service conditions in which the metal is placed. Hydrogen attack, however, is a high temperature phenomenon that is usually associated with hostile service conditions. Diffusional mechanisms play a major role in all forms of hydrogen damage. In almost all cases, it is the precipitation of hydrogen that leads to damage.

References

Craig, Bruce. <u>Metals Handbook, Vol. 13, Corrosion, 9th Edition</u>. Metals Park, OH. ASM International, p. 163, 1986.

Hertzberg, Richard W. <u>Deformation and Fracture Mechanics of Engineering Materials</u>. New York: John Wiley & Sons, Inc., 1996.

Jones, Denny A. <u>Principles and Prevention of Corrosion</u>. New Jersey: Prentice Hall, 1996.

Kim, C.D. <u>Metals Handbook, Vol. 11, Failure Analysis, 9th Edition</u>. Metals Park, OH: ASM International, p. 245, 1986.

Kobrin, G. <u>Metals Handbook, Vol. 13, Corrosion, 9th Edition</u>. Metals Park, OH. ASM International, p. 321, 1986.

Ritchie, R.O. "Subcritical Crack Growth". Material Science 113 Lecture, November 9th, 2000.

Raymond, Louis. <u>Hydrogen Embrittlement: Prevention and Control</u>. Philadelphia, PA. ASTM, 1988.

Turnbull, Alan. <u>Hydrogen Transport & Cracking in Metals</u>. Cambridge, UK. The Institute of Materials, 1995.