Hydrogen Damage and Embrittlement

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HYDROGEN DAMAGE is a term used to designate a number of processes in metals by which the load-carrying capacity of the metal is reduced due to the presence of hydrogen. The detrimental effects of hydrogen on metals are often enhanced when the hydrogen is present in combination with residual or applied tensile stresses. Many types of hydrogen damage are not due to corrosion processes at all. However, because hydrogen damage has many similarities regardless of the source of the hydrogen, damage processes caused by corrosion and manufacturing problems are both described in this article.

Many metals and alloys are susceptible to hydrogen damage; however, specific forms of hydrogen damage are generally more common within particular alloy systems. Hydrogen damage in one form or another can severely restrict the use of certain materials.

This article is divided into three parts. The first part is an introduction to the general forms of hydrogen damage, and the second part is an overview of the different types of hydrogen damage in all the major commercial alloy systems. These two sections cover the broader topic of hydrogen damage, which can be quite complex and technical in nature. The third part focuses on failure analysis where hydrogen embrittlement of a steel component is suspected. Many of the types of parts that were commonly diagnosed with hydrogen embrittlement in the 1980s and 1990s were low-cost commodity products, such as self-tapping screws and small spring clips. The financial resources available to perform a failure analysis in such cases are often limited, if nobody was injured. Therefore, the third section gives practical advice for the failure analysis practitioner or for someone who is contemplating procurement of a cost-effective failure analysis of commodity-grade components suspected of hydrogen embrittlement. Because of the wide economic impact in commodity-grade components, it is worthwhile to look at failure analysis for this specific type of hydrogen damage. This section of the article is written for engineering managers, quality engineers, design engineers, and manufacturing engineers and technicians. Some prevention strategies for design and manufacturing problem-induced hydrogen embrittlement are also provided.

Overview of Hydrogen Damage Processes

Hydrogen is known to cause various problems in many metals and is readily available during the production, processing, and service of metals from operations such as:

- Refining (precipitates upon solidification from supersaturated concentrations)
- Acid cleaning (pickling)
- Electroplating
- Contact with water or other hydrogen-containing liquids or gases
- Other forms of corrosion (e.g., localized corrosion)

Depending on the type of hydrogen-metal interaction, hydrogen damage of metal manifests itself in one of several ways. The types of interactions between hydrogen and metals include the formation of solid solutions of hydrogen in metals, molecular hydrogen, gaseous products from reactions between hydrogen and alloying or segregated impurity elements, or brittle intermetallic hydride compounds.

Specific types of hydrogen damage, some of which occur only in specific alloys under specific conditions (Table 1), are classified in this article as:

- Hydrogen embrittlement
- Hydrogen-induced blistering
- Cracking from precipitation of internal hydrogen
- Hydrogen attack
- Cracking from hydride formation

The first three types are usually observed at ambient temperatures and are closely related to one another. Hydrogen damage usually manifests itself as hydrogen embrittlement in high-strength steels and as hydrogen-induced blistering in low-strength steels. The solubility and diffusivity of hydrogen in steel sharply decrease with lowering temperatures; therefore, when a heavy section of steel containing hydrogen at elevated temperature is rapidly cooled to ambient temperature, the hydrogen remaining in the steel precipitates out in the gaseous state. The pressure of the hydrogen gas is often great enough to produce internal cracks. Hydrogen attack is an elevated-temperature phenomenon, in which hydrogen reacts with metal substrates or alloy additions. A number of transition and rare earth metals form hydrides, and the formation of metal hydrides can result in cracking.

Hydrogen damage is a complex phenomenon that takes on several forms, and many mechanisms have been proposed, which include (Ref 1):

- Hydrogen pressure theory
- Reduced surface energy (surface adsorption) theory
- Decohesion theory
- Enhanced plastic flow theory
- Decarburization (hydrogen attack)
- Hydride formation

The pressure theory assumes that embrittlement is caused by the pressure exerted by gaseous hydrogen on the crack front. For example, when steel is saturated with hydrogen at elevated temperature and then is cooled, gaseous hydrogen precipitates in microvoids, and an extremely high pressure of the gas can be developed. Flakes in heavy forgings and underbead cracks in weldments can be explained by the pressure theory. Hydrogen charged into steel during aqueous corrosion or cathodic charging can also produce a very high pressure at the surfaces of closed voids or pores.

The reduced surface energy theory states that the absorption of hydrogen decreases the surface free energy of the metal and enhances crack propagation. This theory may explain the crack propagation of high-strength steels in low-pressure gaseous hydrogen. The decohesion theory (Ref 2) holds that dissolved hydrogen tends to migrate toward regions of hydrostatic (often termed as triaxial) tensile stress and weakens the material by lowering the bond strength between metal atoms. This theory is the one that is most applicable to the type of hydrogen embrittlement generally

Table 1 Specific types of hydrogen damage

Specific damage process/ mechanism	Most common in	Comments
Hydrogen embrittlement	High-strength steels and heavily cold-worked low-carbon steels, ambient temperatures	Needs sustained stress. Not relevant for impact-induced cracking
Hydrogen-induced blistering	Low-strength steels at ambient temperatures	Hydrogen forms gas-filled blisters
Cracking from precipitation of internal gaseous hydrogen	Heavy steel sections	Induced by high-temperature exposure followed by rapid cooling
Hydrogen attack	Steels subject to combined high-temperature and high-pressure hydrogen. Also affects copper	Irreversible chemical reactions of hydrogen with matrix or alloy elements form high-pressure pockets of gases other than molecular hydrogen.
Cracking from hydride formation	Transition, rare earth, alkaline-earth metals, and their alloys (includes titanium, tantalum, zirconium, uranium, and thorium)	Brittle hydrides often form preferentially where the stress is highest.

found in newly processed parts that crack during shipping or are found cracked at some point during the assembly process. Grain boundaries of steel are particularly sensitive to this type of atomic bond weakening.

The enhanced plastic flow theory is based on fractographic evidence, where the grain facets of intergranular fracture after hydrogen stress cracking reveal dimples at high magnifications (1000 to 5000×). This, however, is complicated by the influence of grain-boundary precipitates, which may act as sites for nucleation of both voids and hydrogen during its migration in grain boundaries. The formation of methane gas bubbles at grain boundaries is another mechanism (see, for example, Fig. 4 in the article "Intergranular Fracture" in this Volume). For titanium alloys, the repeated formation and rupture of the brittle hydride phase at the crack tip is the dominant mechanism. Probably no one mechanism is applicable to all metals, and several mechanisms may operate simultaneously to embrittle a material. Whatever the mechanism, the end result is an adverse effect on the mechanical properties of the material.

Hydrogen Embrittlement

Hydrogen embrittles several metals and alloys, and the effects can range from a slight decrease in the percent reduction of area at fracture to a brittle macroscopic fracture at a relatively low applied stress (often well below the yield strength). Even small amounts of hydrogen can have a deleterious effect, particularly for high-strength steels with tensile strengths of 1240 MPa (180 ksi) or more. A few parts per million of hydrogen dissolved in steel can cause hairline cracking and loss of tensile ductility. Even when the quantity of gas in solution is too small to reduce tension-test ductility, hydrogen-induced delayed fracture may occur.

Although hydrogen embrittlement has been evaluated extensively, it takes on several forms. The various forms or manifestations of

hydrogen embrittlement and the terminology associated with it can be very confusing, because the term has been used without clarified definitions. One classification breaks hydrogen embrittlement into three types (Ref 3, 4):

- Internal reversible hydrogen embrittlement
- Hydrogen environment embrittlement
- Hydrogen reaction embrittlement

This division is roughly equivalent to the classification of hydrogen embrittlement in steels that is defined in *Properties and Selection: Irons, Steels, and High-Performance Alloys*, Volume 1 of *ASM Handbook*, 1990, as (Ref 5):

- Hydrogen environmental embrittlement
- Hydrogen stress cracking (HSC)
- Loss in tensile ductility

This latter division focuses on the mechanical effects of HSC and loss of ductility from reversible hydrogen embrittlement, as opposed to the other categories that are based more on the nature of hydrogen. Either approach could be considered, but this article considers the former based on Ref 4.

Internal Reversible Hydrogen Embrittlement

Internal reversible hydrogen embrittlement has also been termed slow strain-rate embrittlement and delayed failure. The mechanical effects, as described subsequently, may range from loss of ductility to cracking. To be fully reversible, of course, embrittlement must occur without the hydrogen undergoing any type of chemical reaction or causing microscopic cracks to be initiated.

Internal reversible hydrogen embrittlement can occur after a very small average concentration of hydrogen has been absorbed from the environment. However, local concentrations of hydrogen may be substantially greater than average bulk values, because the absorbed hydrogen diffuses into grains or (as is more likely) preferentially into the grain boundary.

Degradation is enhanced by slow strain rates, which thus suggests time-dependent diffusion as a controlling factor. Moreover, embrittlement is usually most severe at room temperature during either sustained stresses or slow strain-rate tension testing. Higher temperatures cause hydrogen to diffuse away from areas of localized concentration. The effect of hydrogen is also strongly influenced by other variables, such as:

- Strength (or hardness) level of the alloy
- Microstructure
- Magnitude of the applied stress
- Presence of a localized triaxial tensile stress
- Amount of prior cold work
- Degree of segregation of tensile low-melting-point elements such as phosphorus, sulfur, nitrogen, tin, or antimony at the grain boundaries

This is the classical type of hydrogen embrittlement. Its unique aspect is the delayed nature of the fractures; that is, after a specimen is charged with hydrogen, fracture does not occur instantly but only after the passage of a certain amount of time. This time-dependent nature (incubation period) for embrittlement by hydrogen is also why it is most noticeable at low strain rates. Internal reversible hydrogen embrittlement has also been observed in a wide variety of other materials, including nickel-base alloys and austenitic stainless steels, provided they are severely charged with hydrogen. However, most attention has been given to the delayed cracking under stress of high-strength steel components exposed to hydrogen from processing treatments such as electroplating, pickling, and other sources. In steels, a few parts per million of dissolved hydrogen can cause hairline cracking and loss of tensile ductility. While hydrogen embrittlement causes strength reduction along with reduced ductility, the hardness remains the same.

Loss of Tensile Ductility

The loss of tensile ductility, one of the earliest documented forms of hydrogen damage, occurs in steels and other alloys exposed to hydrogen. It generally affects lower-strength alloys. Fracture does not necessarily occur, as it does with higher-strength alloys; these alloys experience only a decrease in tensile elongation and reduction in area, depending on strain rate and hydrogen content. This type of embrittlement in steel is reversible; that is, ductility can be restored by relieving the applied stress and aging at room temperature, provided microscopic cracks have not yet initiated.

Hydrogen Stress Cracking

Hydrogen stress cracking is characterized by the brittle fracture of an alloy due to hydrogen exposure from either some time prior to manufacturing or from environmental hydrogen. It is also commonly considered a subcritical crack growth mechanism that often produces

time-delayed fractures in production parts (especially high-strength steels) even with no externally applied stress. The phenomenon is characterized by the simultaneous interactions of sustained static or very slowly changing loads on susceptible materials that have internal dissolved atomic hydrogen.

Hydrogen stress cracking involves the absorption of hydrogen, followed by hydrogen diffusion to regions of high tensile stress, particularly those associated with notches. Because it is a diffusion-controlled process, more slowly applied stresses and, in particular, sustained or static stresses are more likely to allow the hydrogen embrittlement problem to manifest. This gives hydrogen more time to diffuse to the potential crack plane(s). Thus, there is a delay time, or incubation time, before cracking occurs. In this regard, HSC has also been referred to as static fatigue, sustained-load cracking, or hydrogen-induced delayed fracture.

This type of hydrogen damage occurs most often in high-strength steels (tensile strength in excess of approximately 1240 MPa, or 180 ksi), although it can also occur in relatively soft steels that have been heavily cold formed or cold worked. The factors that influence the likelihood of cracking include the hardness or strength level, stress level, the duration of the sustained load, and the concentration of hydrogen. The cracking is most prevalent at ambient temperature, and it can occur under load when the quantity of gas in solution is too small to reduce ductility. The cracking tendency decreases with increasing temperature, and the hydrogen embrittlement phenomenon virtually disappears in steels above 200 °C (390 °F).

Cracks typically initiate internally, usually below the root of a notch at a region of maximum localized tensile triaxial stress. Tensile residual stresses may also promote the initiation of HSC. Crack branching is much less prevalent in hydrogen embrittlement than in stress-corrosion cracking. The crack path is often intergranular, especially for high-strength steels. However, hydrogen-induced fractures are not always intergranular (Ref 5). In high-strength steels, cracking is often intergranular, but transgranular cleavage is also observed. For ductile low-strength steels, the fracture mode is ductile, with decreases in the dimple size.

Cracking Threshold

For an alloy exhibiting a specific strength level and microstructure, there is a stress-intensity value, K_I, below which, for all practical purposes, hydrogen embrittlement cracking does not occur. This threshold crack tip stress-intensity factor (K_{th}) is an experimentally determined quantity that depends on:

- Nominal strength of the unembrittled part
- Amount of hydrogen present in the steel
- Location of the hydrogen in the microstructure
- Presence of other embrittling elements or microstructural phases

The actual value of the tensile stress that creates a crack in a particular component depends on these factors. For example, prior temper embrittlement of high-strength alloy steels enhances HSC. The threshold stress intensity for crack growth is lowered, and intergranular fractures occur. The influence of temper embrittlement on HSC is particularly pronounced as the yield strength is decreased (Ref 5). Very low-impurity-content steels do show high threshold stress-intensity values and freedom from intergranular fracture (Ref 6).

Hydrogen from Preservice Pickling and Electroplating

As noted, HSC can occur from hydrogen pickup from manufacturing. Properly performed pickling alone is not usually a direct cause of hydrogen damage (unless internal voids or other imperfections lead to local formation of atomic hydrogen), because much of the absorbed hydrogen diffuses out of the metal shortly after it is absorbed. Heating at 150 to 200 °C (300 to 390 °F) hastens the removal of hydrogen. Also, the addition of suitable inhibitors to the pickling solution eliminates or minimizes attack on the metal and the consequent generation of nascent hydrogen. Salt baths operated at approximately 210 °C (410 °F) can be used for descaling titanium alloys, superalloys, and refractory metals to avoid the possibility of hydrogen charging associated with pickling.

Plating solutions and plating conditions selected to produce a high-cathode efficiency minimize the amount of hydrogen generated on the metal surface. Because the metallic coatings plated on metal often prevent the hydrogen from leaving the base metal, elevated-temperature baking after plating is generally required to allow the hydrogen to move to microstructural positions in the part interior that are less damaging to the atomic bonds of the iron matrix.

In one hydrogen-damage failure caused by improper baking after electroplating, several cadmium-plated American Iron and Steel Institute (AISI) 8740 steel nuts cracked in seven days after installation on an aircraft wing structure (Fig. 1). Examination of the fracture surface (Fig. 2) showed predominantly intergranular fracture typical of hydrogen embrittlement. The nuts had not been baked for a sufficient time; thus, hydrogen picked up during the plating process was not given sufficient time to diffuse out of the components.

A more recent example is the posttensioning bolts used in the construction of the Bay Bridge in San Francisco, California. High-strength steel was hot dip galvanized for corrosion protection. The bolts started failing in a brittle manner shortly after application of the posttension load, which was attributed to rapid corrosion of the zinc coating and hydrogen generation while exposed to water, causing hydrogen embrittlement and eventual fracture. These bolts had to be replaced with an

Fig. 1 Cadmium-plated AISI 8740 steel nut that failed by hydrogen embrittlement. Failure occurred seven days after installation on an aircraft wing structure. See also Fig. 2. Original magnification: 5×. Courtesy of Lockheed-Georgia Company

alternative fastening method at great cost and effort (Ref 7, 8).

Procedures for prevention of hydrogen damage in electroplating and preparation for electroplating are described in ASTM A 143, "Standard Practice for Safeguarding against Embrittlement of Hot Dip Galvanized Structural Steel Products and Procedure for Detecting Embrittlement." Other relevant standards include:

- ASTM F 1940, "Standard Test Method for Process Control Verification to Prevent Hydrogen Embrittlement in Plated or Coated Fasteners"
- ASTM F 519, "Standard Test Method for Mechanical Hydrogen Embrittlement Evaluation of Plating Processes and Service Environments"
- ASTM G 142, "Standard Test Method for Determination of Susceptibility of Metals to Embrittlement in Hydrogen-Containing Environments at High Pressure, High Temperature, or Both"
- ASTM F 1459, "Standard Test Method for Determination of the Susceptibility of Metallic Materials to Gaseous Hydrogen Embrittlement"

Hydrogen Environmental Embrittlement

Hydrogen embrittlement, in classic form, is reversible, in that the damage should be eliminated by removing the hydrogen. However, hydrogen can also cause permanent damage from exposure to environmental hydrogen during service. Gaseous environments containing hydrogen are also damaging. Hairline cracking usually follows prior-austenite grain boundaries and seems to occur when the damaging effect of dissolved hydrogen is superimposed

on the stresses that accompany the austenite-to-martensite transformation. Hairline cracking is readily recognized by metallography and is most common near the center of fairly bulky components, where constraint of plastic deformation is high. Affected areas are recognized on fracture surfaces by their brittle appearance and high reflectivity, which usually contrasts with the matte appearance of surrounding regions of ductile fracture. This has led to such areas being described as flakes or fisheyes. These and other forms of hydrogen damage are described in subsequent sections on blistering, precipitation of internal hydrogen, hydrogen attack, and hydride formation.

However, in terms of the various types of in-service environments, hydrogen embrittlement can also occur. This type of situation may be complicated by more factors than the preservice type of delayed HSC. In particular, hydrogen from corrosion reactions may be a factor, or stress-corrosion cracking (SCC) mechanisms may be involved. In particular, the distinction between SCC and hydrogen embrittlement can be difficult. However, the distinction is well defined in terms of electrochemical potentials (Fig. 3) (Ref 9), where hydrogen embrittlement occurs in a lower region associated with hydrogen formation. Current mechanisms of corrosion-assisted, sustained-load cracking are variations of two basic theories: crack advance by anodic dissolution or hydrogen embrittlement. The controlling factors in these two are:

Anodic dissolution (SCC) is characterized by:

- Grain-boundary precipitate size, spacing, and/or volume fraction
- Grain-boundary precipitate-free zone width, solute profile, or deformation mode
- Matrix precipitate size/distribution and deformation mode
- Oxide rupture and repassivation kinetics

Hydrogen embrittlement is characterized by:

- Hydrogen absorption leading to grain-boundary or transgranular decohesion
- Internal void formation via gas pressurization
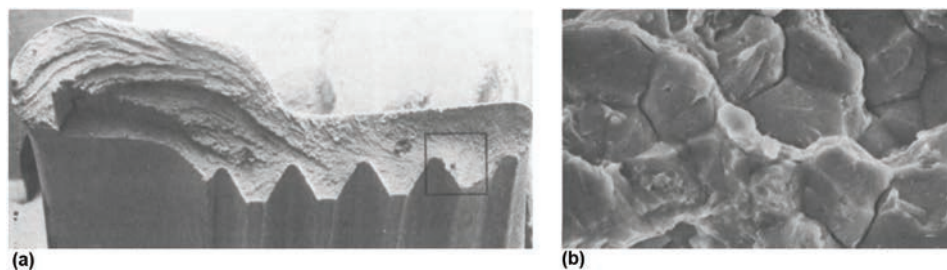- Enhanced plasticity (adsorption and absorption arguments exist)

Hydrogen embrittlement and SCC are also sometimes distinguished in terms of application and the source of the hydrogen atoms. If the hydrogen is coming from an intentional manufacturing process, and that hydrogen facilitates cracking at lower-than-expected stresses, whether the hydrogen production itself is intentional or not, the term *hydrogen embrittlement* is used.

Regardless of the definition, environmental factors causing the cracking must be properly evaluated, and obviously, in-service conditions may involve more environmental factors than hydrogen charging during manufacturing. Therefore, the electrochemical definition of hydrogen embrittlement (Fig. 3) has more specificity for complex environmental conditions in service.

In-Service Cracking from Hydrogen Charging in an Aqueous Environment

When a metal or a metal alloy corrodes in a low-pH solution, the cathodic partial reaction is reduction of the hydrogen ion. Although most of the reduced hydrogen reacts to form H_2 and leaves the metal surface as gaseous hydrogen, a part of the reduced hydrogen enters into the metal as atomic hydrogen. The presence of certain chemical substances that prevent the recombination of hydrogen to form molecular hydrogen enhances the absorption of nascent (atomic) hydrogen into the metal. These substances are called cathodic poisons, and they include phosphorus, arsenic, antimony, sulfur, selenium, tellurium, and cyanide ion. Among the cathodic poisons, sulfides are among the most common. Environments containing hydrogen sulfide can cause severe embrittlement of steels and some other high-strength alloys. On the other hand, corrosion inhibitors lower the corrosion rate and thus the amount of hydrogen charged into the metal.

In-Service Atmospheric and Aqueous Corrosion

Most high-strength steels are susceptible to hydrogen embrittlement when they are stressed and exposed to fresh or sea water and even during atmospheric exposure. The susceptibility of steels to hydrogen embrittlement generally increases with increasing tensile strength.

Steels having a tensile strength greater than approximately 1000 MPa (150 ksi) are susceptible to embrittlement. Above a tensile strength level of 1250 MPa (180 ksi), most alloy steels, such as AISI 4130 and 4340, and precipitation-hardening stainless steels are susceptible to hydrogen embrittlement cracking in marine atmospheres when the residual or applied tensile stresses are sufficiently high. The cracking occurs after some time has passed. Steels with tensile strengths less than 690 MPa (100 ksi) appear to be much more resistant to hydrogen embrittlement cracking, and the structures made with such steels have been used in service without serious problems in various environments, as long as they do not contain hydrogen sulfide.

As noted, hydrogen embrittlement cracking of high-strength steel in aqueous environments may be sometimes erroneously called SCC. Cracking of high-strength steel in aqueous environments is caused by hydrogen absorbed into the steel during corrosion. It is not caused by an anodic dissolution mechanism, such as the chloride SCC of austenitic stainless steels or caustic cracking of low-alloy steels. The analyst should bear in mind, however, that sometimes the boundary between SCC and hydrogen embrittlement may not be very clear, depending on the understanding of the physics, chemistry, and metallurgy of a particular situation. The more important concern for most failure analysts or their clients or internal customers is whether the investigation can provide insight on prevention strategies.

When working on failure analysis cases involving hydrogen damage, it is important to realize that the electrochemical conditions at the tip of a pit or an advancing crack are not the same as those of the bulk solution. This is because the solution chemistry in the region of the pit or crack tip may be quite different from that of the bulk solution. In a laboratory
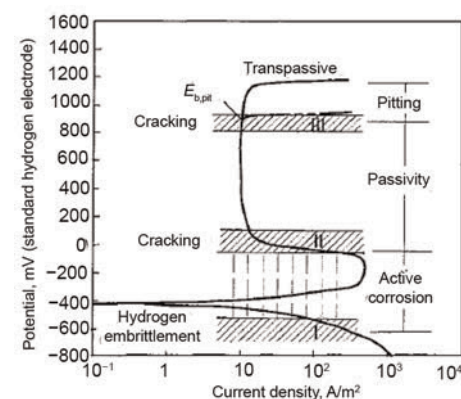

Fig. 2 Fracture surface of failed cadmium-plated nut in Fig. 1. (a) Macrograph of fracture surface. Original magnification: 15×. (b) Scanning electron micrograph of the area in the box in (a) showing typical intergranular fracture. Original magnification: 3950×. Courtesy of Lockheed-Georgia Company

Fig. 3 Potential ranges of environmentally assisted cracking by (I) hydrogen embrittlement, (II) cracking of unstable passive film, and (III) cracking initiated at pits near the pitting potential. Vertical dashed lines define potential range over which nonpassivating films may crack under stress. Source: Ref 9

study, when wedge-opening loading specimens were exposed to sodium chloride solutions, the pH value of the solution at the crack tip was measured to be approximately 3.5, regardless of that of the bulk solution. At the crack tip, where diffusion is limited, the pH value of the solution is lowered by the acidic hydrolysis reaction, and in such a low-pH solution, the cathodic partial reaction is the reduction of the hydrogen ion. As a result, nascent hydrogen is generated at the tip of the pit or crack and absorbed into the metal. It has also been shown that hydrogen can be generated at the crack tip even when an anodic potential is applied to the bulk metal.

In-Service Failures in Environments Containing Hydrogen Sulfide (Sulfide Stress Cracking)

High-strength steel pipes used in drilling and completion of oil and gas wells may exhibit delayed cracking in environments containing hydrogen sulfide. This type of fracture is referred to as sulfide stress cracking. The basic cause of sulfide stress cracking is embrittlement resulting from hydrogen absorbed into steel during corrosion in sour environments. The presence of hydrogen sulfide in the environment promotes hydrogen absorption into steel, thereby making the environment more severe and thus more likely to cause hydrogen embrittlement. Although hydrogen sulfide gas, like gaseous hydrogen, can cause embrittlement, water ordinarily must be present for sulfide stress cracking to occur.

The susceptibility to sulfide stress cracking increases with increasing hydrogen sulfide concentration or partial pressure and decreases with increasing pH. The ability of the environment to cause sulfide stress cracking decreases markedly above pH 8 and below 100 Pa (~0.001 atm) partial pressure of hydrogen sulfide. The cracking tendency is most pronounced at ambient temperature and decreases with increasing temperature. For a given strength level, tempered martensitic steels have better sulfide stress cracking resistance than normalized-and-tempered steels, which in turn are more resistant than normalized steels. Untempered martensite demonstrates poor resistance to sulfide stress cracking. It is generally agreed that a uniform microstructure of fully tempered martensite is desirable for sulfide stress cracking resistance.

Researchers in sulfide stress cracking are not in agreement as to the effect of alloying elements on the sulfide stress cracking resistance of carbon and low-alloy steels, with the exception of one element—nickel—which is detrimental to sulfide stress cracking resistance. Steels containing more than 1% Ni are not recommended for service in sour environments.

Welds and associated heat-affected zones are often less resistant to sulfide stress cracking than the adjacent base metal. The high hardness and residual stresses resulting from welding are believed to increase the susceptibility. In a laboratory study of the sulfide stress cracking resistance of submerged arc weldments in a hydrogen-sulfide-saturated aqueous solution of 0.5% acetic acid and 5% sodium chloride, no failures were observed for the welds with hardness values below 191 HB (91 HRB); all of the welds with hardness values of 225 HB (20 HRC) or higher cracked. Steels with hardness values less than 22 HRC are considered acceptable for sour service. Metallic materials resistant to sulfide stress cracking for oil-field equipment are covered in ANSI/NACE MR0175/ISO 15156, "Petroleum and Natural Gas Industries—Materials for Use in H_2S-Containing Environments in Oil and Gas Production."

In-Service Cathodic-Protection-Related Damage

Marine structures and underground pipelines are cathodically protected either with sacrificial anodes or with impressed current. Although the cathodic protection of such structures usually does not cause hydrogen embrittlement, high-strength steel can be embrittled by cathodic protection. Cathodic protection is not recommended for high strength steel components of any kind.

In-Service Cracking from Gaseous Hydrogen

Steel vessels and other equipment that contains hydrogen gas at high pressures at ambient temperature are susceptible to fracture by hydrogen embrittlement. Many high-strength steels are subject to severe embrittlement in tension tests conducted in high-pressure hydrogen gas, and the cracking tendency increases with increasing pressure of hydrogen. As has been noted many times in this article for many types of hydrogen damage, the cracking susceptibility of steels in gaseous hydrogen generally increases with increasing hardness.

Generally, high-strength steels and high-strength nickel alloys display severe degradation of tensile properties in hydrogen gas. Austenitic stainless steels, aluminum alloys, and alloy A286 show very little embrittlement in this environment; most other engineering metals and alloys are affected to a lesser degree. Seamless steel vessels have been used for the containment of hydrogen gas at moderately high pressure without any reported problems. When austenitic stainless steels, such as AISI 304L and 309S, are exposed to high-pressure hydrogen gas (69 MPa, or 10 ksi), the macroscopic tensile ductility is markedly reduced, although the microscopic fracture may be dimpled microvoid coalescence. The loss in tensile reduction of area can be correlated with a change in dimple size (Ref 10).

Hydrogen gas at atmospheric pressure can cause embrittlement in martensitic high-strength steels. Subcritical crack growth is observed with high-strength steel at very low stresses in pure hydrogen gas, and oxygen in small quantities stops the crack growth. Oxygen is believed to form an oxide barrier at the crack tip by preferential adsorption, thereby protecting the crack tip from the damaging effects of the hydrogen.

Fracture Characteristics

Crack Origin

When a hydrogen-damage failure is caused by hydrogen embrittlement or hydrogen-induced blistering, the crack typically originates in the interior of the part or very close to the metal surface. In metals of relatively low strength and hardness and in high-strength metals that are not subjected to significant levels of applied or residual tensile stresses, cracking almost always originates in the interior of the metal. In high-strength metals subjected to applied or residual tensile stresses, especially if a severe stress raiser such as a sharp notch is present at the surface, cracking is likely to originate near the surface.

Crack Morphology

A hydrogen-assisted crack is usually a single crack that shows no significant branching (Fig. 4). The crack path can be either intergranular or transgranular, and the crack path sometimes changes from one to the other as it propagates. Intergranular fracture becomes more likely at higher strength and with impurities. When transgranular fracture from hydrogen occurs in less ductile (body-centered cubic, or bcc) alloys, the mechanisms may be brittle cleavage or quasi-cleavage. In more ductile low-strength steels or face-centered cubic (fcc) alloys, fracture may be by dimpled microvoid coalescence. Therefore, the results of metallographic and electron fractographic examinations should be carefully interpreted for failure analysis. Examination at low magnification should precede examination at higher magnifications. Examination of the fracture surface at high magnifications (1000× or more) may yield clues on the potential mechanisms of intergranular fracture in the grain boundaries. Often, an originally brittle crack may transition into ductile behavior as the crack propagates. These different zones (i.e., brittle, transition zone with a mix of brittle and ductile features, and finally a completely ductile tearing zone) can be clearly distinguished during fractographic examination.

Deposits on the Fracture Surface

Corrosion products are ordinarily not present on the surface of hydrogen-damaged fractures, unless the surfaces have been exposed to corrosive environments. Foreign matter, if present, is in trace amounts only, unless the fracture surfaces had been exposed to contaminants. Energy-dispersive x-ray spectroscopy allows the determination of the elements on the fracture surface.

Laboratory Cracking Tests

Laboratory cracking tests are used to verify that the material is susceptible to hydrogen damage under a given environmental condition or to distinguish between hydrogen damage and SCC. One method of distinguishing between hydrogen embrittlement and SCC is to note the effect of small impressed electric currents on time to failure in a constant-load test. If cracking has occurred by a stress-corrosion mechanism, application of a small anodic current shortens the time to failure. When hydrogen embrittlement is the cracking mechanism, a cathodic current accelerates cracking. Electrochemical methods are also used to determine whether hydrogen can be charged into metal in given solutions.

For example, consider the type 431 stainless steel mushroom-head closure shown in two views in Fig. 4 that fractured in service at a hydrogen pressure of 3×10^8 Pa (3000 atm). Fracture occurred at room temperature after miscellaneous chemical service that included exposures to hydrogen at temperatures from ambient to 350 °C (660 °F). The fracture surface displayed areas of both transgranular cleavage, as shown in the stereo pair of Fig. 5, and intergranular separation, as shown in the stereo pair of Fig. 6, which is characteristic of hydrogen embrittlement of high-stress steels. Debris from the final reaction to which the part was exposed has resulted in artifacts on the transmission electron microscopy replicas, but there appears to be no evidence of grain-boundary corrosion in Fig. 6. This is an important finding, in that it differentiated this intergranular fracture, which was caused by hydrogen embrittlement, from similar ones produced by SCC. Only by meticulous fractographic examination can clues be gained that make it possible to distinguish between these two fracture mechanisms.
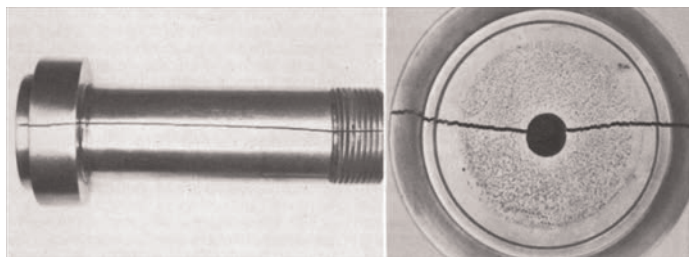

Fig. 4 Two views of a fracture from hydrogen embrittlement of a type 431 stainless steel mushroom-head closure. This is not typical; hydrogen embrittlement cracking on cylinders is usually circumferential.
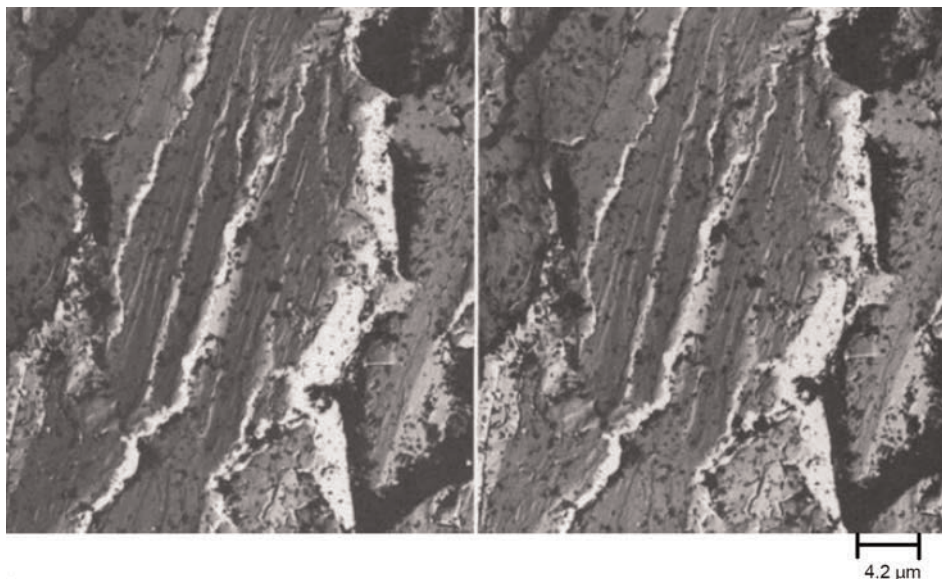

Fig. 5 Transgranular cleavage in an area of the surface of the hydrogen embrittlement fracture of the type 431 stainless steel mushroom-head closure shown in Fig. 4. See also Fig. 6. When viewed in three dimension, this stereo pair shows a massive ridge running from top to bottom at the left, with pronounced cleavage steps on its right-hand slope. The corrosion debris remaining from service and extracted by the replica may be seen projecting from the surface. Transmission electron microscopy; original magnification: 2400×

Hydrogen Reaction Embrittlement

Although the sources of hydrogen may be any of those mentioned previously, this type of embrittlement is quite distinct from hydrogen environment embrittlement. Once hydrogen is absorbed, it may react near the surface or diffuse substantial distances before it reacts. Hydrogen can react with itself, with the matrix, or with a foreign element in the matrix. The chemical reactions that comprise this type of embrittlement or attack are well known and are encountered frequently. The new phases formed by these reactions are usually quite stable, and embrittlement is not reversible during room-temperature aging treatments.

Atomic hydrogen (H) can react with the matrix or with an alloying element to form a hydride (MH_x). Hydride phase formation can be either spontaneous or strain induced. Atomic hydrogen can react with itself to form molecular hydrogen (H_2). This problem is frequently encountered after steel processing and welding; it has been termed flaking or fisheyes. Atomic hydrogen can also react with a foreign element in the matrix to form a gas. A principal example is the reaction with carbon in low-alloy steels to form methane (CH_4) bubbles. Another example is the reaction of atomic hydrogen with oxygen in copper to form steam (H_2O), resulting in blistering and a porous metal component.

Hydrogen-Induced Blistering

Blistering is observed in low-strength steels and other metals. It is caused by atomic hydrogen diffusing to internal defects or inclusions, where it precipitates as molecular (diatomic) hydrogen. This generates substantial pressure, which produces blisters. *Shatter cracks*, *flakes*, and *fisheyes* are terms that describe cracks or the surface appearance of a fracture in castings, forgings, wrought alloys, or weldments. These defects are caused by the presence of excessive hydrogen in the liquid melt prior to solidification. Microperforation may also occur, mainly when steels are exposed to very high-pressure hydrogen near room temperature.

Hydrogen-induced blistering is most prevalent in low-strength alloys, and it is observed in metals that have been exposed to hydrogen-charging conditions, for example, acid pickling or corrosion in environments containing hydrogen sulfide. When hydrogen is absorbed into metal and diffuses inward, it can precipitate as molecular hydrogen at internal voids, laminations, or inclusion/matrix interfaces, and it can build up pressure great enough 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 (Fig. 7). 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. The absorbed hydrogen may come from various sources.
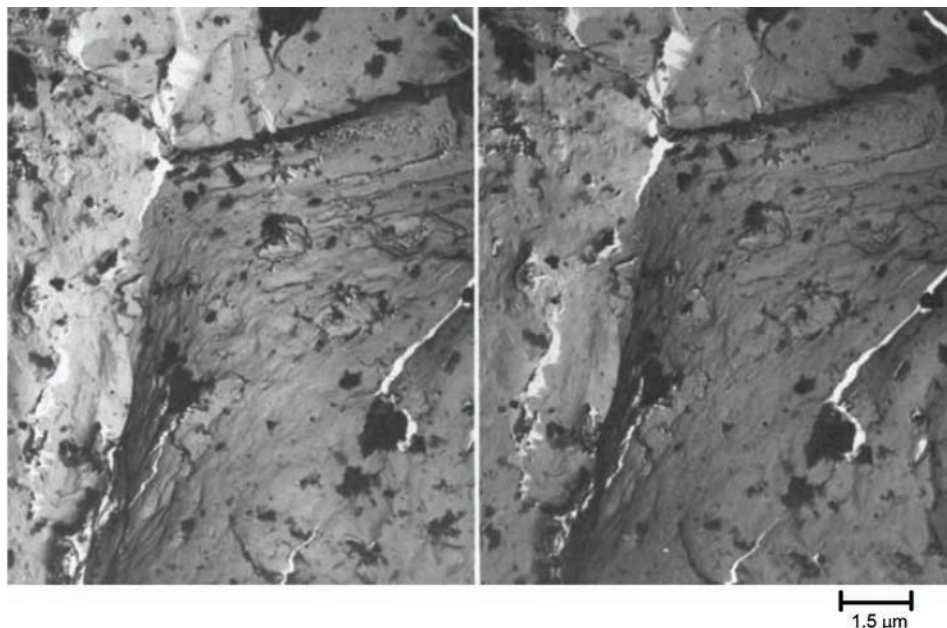
Fig. 6 Intergranular separation in an area of the surface of the hydrogen embrittlement fracture of the type 431 stainless steel mushroom-head closure of Fig. 4 and 5. When viewed in three dimension, the somewhat rounded separated-grain surfaces show cavities akin to dimples in appearance but more probably sites of previous intergranular inclusions. The corrosion debris may be seen projecting from the fracture surfaces. Transmission electron microscopy; original magnification: 6600×

Fig. 7 Hydrogen-induced blistering in a 9.5 mm (3/8 in.) thick carbon steel plate (ASTM A285, grade C) that had been in service one year in a refinery vessel. Original magnification: 1.5×

Fig. 8 Stepwise cracking of a low-strength pipeline steel exposed to hydrogen sulfide (H_2S). Original magnification: 6×

Corrosion-generated hydrogen causes blistering of steel in oil-well equipment and in petroleum-storage and refinery equipment. In the refinery, hydrogen-induced blistering has been found most frequently in vessels handling sour (hydrogen-sulfide-containing) light hydrocarbons and in alkylation units where hydrofluoric acid is used as a catalyst. Storage vessels with sour gasoline and propane are highly prone to blistering, but sour crude storage tanks are less prone to blistering, apparently because the oil film of the heavier hydrocarbons acts as a corrosion inhibitor. In storage vessels, blistering is generally at the bottom or in the vapor space where water is present. Gas-plant vessels in catalytic hydrocarbon-cracking units are particularly prone to blistering, because the cracking reaction generates cyanides. The presence of cyanides, hydrogen sulfide, and water enhances hydrogen absorption into steel. Hydrogen-induced blistering also occurs on steel plates used as cathodes in industrial electrolysis.

Line pipe transmitting wet sour gas can develop hydrogen-induced cracking in the pipe wall. When line-pipe steel is exposed to sour brine in the absence of applied stress, a number of cracks parallel to the longitudinal axis of the pipe may develop through the wall, and the tip of one crack may link up with another in stepwise fashion (Fig. 8). This type of cracking is called stepwise cracking, and it can significantly reduce the effective wall thickness of the pipe. It is believed that a single, straight longitudinal crack is less harmful than stepwise cracks. The presence of hydrogen sulfide in the corrodent greatly promotes the absorption of hydrogen into steel. Thus, the fugacity of hydrogen generated during sulfide corrosion is extremely high—often on the order of 10^3 MPa (10,000 atm).

Hydrogen-induced cracks in line-pipe steels are always associated with certain metallurgical features, such as inclusions, large precipitate particles, or martensite bands. Elongated inclusions, such as type II manganese sulfides and glassy silicates, are particularly detrimental to hydrogen-induced cracking resistance. The oxygen content in molten steel markedly affects the shape of sulfide inclusions in rolled steel. Manganese sulfides in semikilled steel deform to a lesser extent during hot rolling than those in silicon-aluminum-killed steels. Semikilled steels usually contain ellipsoidal manganese sulfides (type I MnS) and generally have better hydrogen-induced cracking resistance than fully killed steels having elongated manganese sulfides (type II MnS). Although the hydrogen-induced cracking resistance of steel increases with decreased sulfur content, lowering the sulfur level alone does not provide immunity to hydrogen-induced cracking. Most modern steels are produced in the killed form, because the usually more-economical continuous casting processes only work for killed steels.

The presence of martensite banding in line-pipe steel increases the susceptibility to hydrogen-induced cracking. The formation of martensite can be controlled by selecting suitable steel compositions and the proper thermomechanical treatment. Addition of approximately 0.3%

Cu is known to improve the hydrogen-induced cracking resistance of steel, but the beneficial effect of copper prevails only in environments with relatively high pH (approximately 5 or more) and diminishes in low-pH (3.5 or less) solutions.

Flakes

Heavy steel forgings often contain a number of hairline cracks in the center part, and such cracks are called flakes. On fracture surfaces, flakes appear as small areas of elliptical bright cracks. Flakes are formed during cooling after the first forging or rolling and not during cooling after solidification. Flakes are caused by localized hydrogen embrittlement resulting from internal hydrogen.

The primary source of hydrogen in steelmaking is moisture in the atmosphere and in the additives, and the hydrogen content of molten steel after refining can be as high as 5 to 8 ppm. Hydrogen dissolves more in the fcc crystal structure than in the bcc crystal structure, and the solubility decreases exponentially with decreasing temperature. The lattice solubility of hydrogen in steel is much smaller than 0.1 ppm at room temperature. Therefore, on cooling, hydrogen precipitates

as molecular hydrogen at inclusions or micropores, and because such regions are already embrittled by hydrogen, flakes are readily formed by the gaseous hydrogen pressure. Flakes form at temperatures below 200 °C (390 °F) and are generally oriented within the forging grain or segregated bands. Flaking sensitivity increases with increasing hydrogen content.

Fisheyes

Another example of localized hydrogen embrittlement, fisheyes describe small, shiny spots occasionally observed on the fracture surface of tension specimens from steel forgings or plates having a high hydrogen content. Fisheyes are associated with reduced tensile ductility. Fractographic examination usually reveals microscopic stress raisers, such as pores or nonmetallic inclusions, within the fisheye. Baking or prolonged room-temperature aging of tension specimens frequently eliminates fisheyes and restores tensile ductility.

When this type of hydrogen damage occurs in welding, it is called underbead cracking. This form of cracking develops in the heat-affected zone (HAZ) of the base metal and runs roughly parallel to the fusion line. Because cracking caused by hydrogen may occur hours or days after welding, it is also known as delayed cracking. The factors controlling this type of cracking are dissolved hydrogen, tensile stress, and low-ductility microstructure, such as martensite. Hydrogen can be transferred to the molten weld pool from the arc atmosphere. Sources of hydrogen include the shielding gas, flux, wet rods, or surface contamination. As the weld metal cools, it becomes supersaturated with hydrogen, which diffuses into the HAZ, which is in a state of high triaxial tensile stress. As the austenite transforms into martensite on rapid cooling, the hydrogen is retained in this region, and, as a result, the metal is embrittled by its presence. The stresses generated by external restraint and by volume changes due to the transformation can easily produce cracks in this region.

Hydrogen Attack

Hydrogen attack occurs at high temperatures rather than at or near room temperature. Hydrogen reacts with carbon or carbides within the steel to form methane gas. This may simply decarburize the steel, lowering its strength, or may produce cracks or fissures. This problem does not occur below 200 °C (390 °F). Steel exposed to high-temperature, high-pressure hydrogen appears to be unaffected for days or months and then suddenly loses its strength and ductility. However, hydrogen attack is different from hydrogen embrittlement. Hydrogen attack is irreversible damage, and it occurs at elevated temperatures, whereas hydrogen embrittlement is often reversible and occurs at temperatures below 200 °C (390 °F).

During hydrogen attack of steel, methane bubbles form along grain boundaries; these bubbles subsequently grow and merge to form fissures. Failure by hydrogen attack is characterized by decarburization and fissuring at grain boundaries (Fig. 9) or by bubbles in the metal matrix. This type of hydrogen damage is most commonly experienced in steels that are subjected to elevated temperatures in petrochemical-plant equipment that often handles hydrogen and hydrogen-hydrocarbon streams at pressures as high as 21 MPa (3 ksi) and temperatures up to 540 °C (1000 °F).

The severity of hydrogen attack depends on temperature, hydrogen partial pressure, stress level, exposure time, and steel composition. Additions of chromium and molybdenum to the steel composition improve the resistance to hydrogen attack. On the basis of industrial experience, the American Petroleum Institute prepared a materials selection guide for hydrogen service at elevated temperatures and pressures (Ref 11). This is known as the Nelson diagram, and it is very useful for proper selection of materials for high-temperature hydrogen service.

Moisture in hydrogen enhances decarburization of steel. Hydrogen gas with a dewpoint of −45 °C (−50 °F) does not decarburize hypoeutectoid steels. Also, the decarburization effect of hydrogen on these steels at temperatures below 700 °C (1290 °F) is negligible. Although hydrogen can severely decarburize steel under certain conditions of temperature and dewpoint, decarburization is not limited to hydrogen atmospheres only, and it may occur in a variety of hydrogen-free heat treatment atmospheres, such as oxygen, air, and carbon dioxide, and in molten salt baths.

Damage by hydrogen embrittlement or blistering may also occur in steel after rapid cooling after prolonged exposure to high-temperature, high-pressure hydrogen. The excess hydrogen cannot then escape during cooling and causes cracking or blistering.

Hydrogen attack can also occur in copper. At elevated temperature, hydrogen absorbed in tough pitch copper internally reduces Cu_2O particles present in the copper, forming pockets of steam. Because water vapor cannot diffuse away, the steam pressure in the pockets can be very high, causing cavities or blisters. Similar behavior can occur in silver.

Cracking from Hydride Formation

A number of transition, rare earth, alkaline-earth metals, and the alloys of these metals are subject to embrittlement and cracking due to hydride formation. Among these metals, the commercially important ones are titanium, tantalum, zirconium, uranium, thorium, and their alloys. The presence of hydrides in these metals can cause significant increases in laboratory-measured strength and large losses in ductility and toughness. As in other types of alloys, excess hydrogen is readily picked up during melting or welding, and hydride formation takes place during subsequent cooling. The use of vacuum melting and the modification of compositions can reduce susceptibility to hydride formation. Hydrogen can often be removed by annealing in vacuum. Welding generally requires the use of inert gas shielding to minimize hydrogen pickup.

The hydride particles often have the form of platelets and show preferred orientation within the parent lattice, depending primarily on the metal or alloy composition. The large volume change associated with hydride formation leads to a strong interaction between the hydride-formation process and externally applied stresses. Applied stresses can cause preferential alignment of hydrides or realignment. In most cases, the hydride phase has a much lower ductility than the matrix.

Susceptibility of Various Metals

Most metals and alloys are susceptible to hydrogen damage, and many are susceptible to more than one type of hydrogen damage. Carbon and low-alloy steels can fail by several types of hydrogen damage. Failure by hydrogen
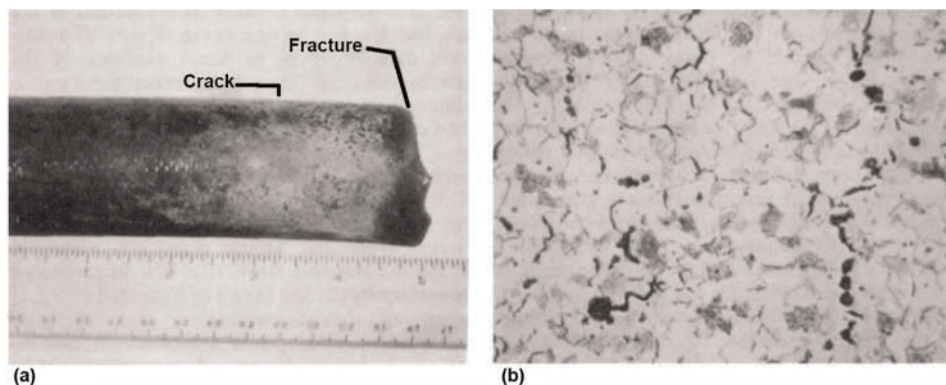

Fig. 9 Section of ASTM A106 carbon steel pipe with wall severely damaged by hydrogen attack. The pipe failed after 15 months of service in hydrogen-rich gas at 34.5 MPa (5000 psig) and 320 °C (610 °F). (a) Overall view of failed pipe section. (b) Microstructure of hydrogen-attacked pipe near the midwall. Hydrogen attack produced grain-boundary fissures that are radially aligned.

embrittlement is often encountered with high-strength steels, especially when the tensile strength is above 1034 MPa (150 ksi). Low-strength steels are considered resistant to hydrogen embrittlement, but they are susceptible to hydrogen-induced blistering. In high-temperature hydrogen environments, carbon and low-alloy steels are also subject to hydrogen attack. However, steels are not susceptible to cracking caused by hydride formation.

Stainless Steels

The susceptibility of the different types of stainless steels (austenitic, ferritic, martensitic, and precipitation hardening) to failure by hydrogen damage varies widely.

Austenitic Stainless Steels

Although austenitic stainless steels are very susceptible to chloride SCC, they are more resistant to hydrogen embrittlement than bcc steels. This may be due to the larger size of the interstitial site in the center of the unit cell. Another factor in the resistance of austenitic stainless steels to hydrogen damage may be the low hydrogen diffusivities in these steels. Hydrogen diffusivity in austenite is several orders of magnitude lower than that in ferrite. However, because the outgassing rate is lower, low-energy trapping of hydrogen can occur in fcc iron-base alloys at imperfections generated by deformation (e.g., dislocations and ε or α martensite) (Ref 2). There is a general correlation between hydrogen resistance and austenite stability.

Ferritic Stainless Steels

In the annealed condition, ferritic stainless steels are very resistant to hydrogen damage, because of their low hardness. However, in the cold-worked or as-welded condition, ferritic stainless steels are susceptible to hydrogen embrittlement.

Martensitic and Precipitation-Hardening Stainless Steels

These steels have high strength and are subject to hydrogen embrittlement. The susceptibility to cracking increases with increasing yield strength, and almost any corrosive environment can cause failure by hydrogen embrittlement in these types of stainless steels. Even a mild environment, such as fresh water at room temperature, may cause cracking in especially susceptible alloys. In one case, for example, a precision bolt of 17-4 PH (type 630) stainless steel cracked from hydrogen embrittlement when exposed for approximately nine months in a warm seacoast atmosphere while in contact with 7075 aluminum alloy (Ref 12).

Nickel-Base Alloys

Hydrogen embrittlement of nickel-base alloys is exemplified by three forms: brittle (usually intergranular) delayed fracture, a loss in reduction of area while often retaining a microvoid coalescent fracture, or a reduction in properties such as fatigue strength. Although cleavage-type cracks have been reported in nickel-base alloys, they are not the predominant mode of fracture. Table 2 lists alloys and environments in which hydrogen embrittlement is known to occur.

Annealed Nickel Alloys

With few exceptions, fully annealed nickel-base alloys are essentially immune to hydrogen-induced delayed failure, but alloy B-2 is susceptible to hydrogen embrittlement in H$_2$S-containing environments even in the annealed condition. Some nickel alloys do not show significant susceptibility to hydrogen embrittlement. These alloys include alloys 825, G and G-3, and alloy 20Cb3, as well as austenitic nickel-base alloys with correspondingly high iron contents.

Large reductions in the ductility of nickel-base alloys due to hydrogen embrittlement have been observed at strain rates near 10^{-4} to 10^{-6} s^{-1}. Only when the strength level of the alloys is increased by cold working or by heat treatment is the incidence of hydrogen embrittlement significant. Also, only the low-iron-containing alloys (generally less than 10% Fe) are significantly affected by hydrogen-induced delayed fracture.

The fracture mode may remain microvoid coalescence, but annealed nickel has been shown to be susceptible to intergranular hydrogen embrittlement. This phenomenon of intergranular fracture appears to be related to the sulfur content/segregation in nickel.

Nickel-Base Superalloys

In general, hydrogen embrittlement has not been a serious problem with heat-resistant alloys. However, laboratory tests have shown that certain nickel-base alloys are susceptible to embrittlement when exposed to highly oxidizing environments or to pure hydrogen at a pressure of 34 MPa (5 ksi) and a temperature of 680 °C (1250 °F). The susceptibility of precipitation-hardenable alloys, such as alloys X-750, alloy K-500, alloy IN-718, and Incoloy 945/945X, has been reported from laboratory tests and from field exposures with less susceptibility at lower strength levels. Some of the solid-solution alloys, such as alloy C-276 and alloy 625, are susceptible to hydrogen embrittlement under conditions of hydrogen charging when cold worked to high strength levels. Aging at temperatures (540 °C, or 1000 °F) at which ordering and/or grain-boundary segregation can occur greatly increases this susceptibility to hydrogen embrittlement.

Aluminum and Aluminum Alloys

Hydrogen damage occurs occasionally in aluminum and aluminum alloys, but it is not usually a serious problem. When a high-strength aluminum alloy is cathodically charged, its ductility is reduced. Hydrogen embrittlement of aluminum alloys can result in intergranular or transgranular cracking. Dry hydrogen gas does not cause significant hydrogen embrittlement in aluminum alloys, but Environmentally Assisted Cracking (EAC) of Al-Zn-Mg alloys in most gases is considered hydrogen embrittlement. Problems with hydrogen in aluminum alloys arise mostly from formation of gas-filled voids during solidification. These voids can affect both cast and wrought products. In ingots for wrought products, the presence of hydrogen gas in voids inhibits healing on subsequent working and is responsible for such defects as bright flakes in thick sections and blisters on the surface of annealed or heat treated material. The principal effect of bright flakes is a reduction in short-transverse ductility.

Copper and Copper Alloys

Copper and its alloys are not susceptible to attack by hydrogen, unless they contain copper oxide. Tough pitch coppers, such as C11000, contain small quantities of Cu$_2$O. Deoxidized coppers with low residual deoxidizer contents—C12000, for example—may contain Cu$_2$O but contain less than tough pitch coppers. These deoxidized coppers are not immune to hydrogen embrittlement.

Deoxidized coppers with high residual deoxidizer contents, however, are not susceptible to hydrogen embrittlement, because the oxygen is tied up in complex oxides that do not react appreciably with hydrogen.

Titanium and Titanium Alloys

Hydrogen damage in titanium alloys results from embrittlement caused by absorbed

Table 2 Nickel-base alloys exhibiting hydrogen embrittlement

Alloy	Environment
600	Cathodic charge/tensile test
C-276, C-4, MP35N, 625, 718	⋯
Pure nickel	Cathodic charge H$_2$SO$_4$
K500	Sour oil and gas environment
X750	5% NaCl + 5% CH$_3$COOH + H$_2$S
718, A286, 625	Hydrogen gas (34 MPa, or 5000 psi) charged at room temperature
Pure nickel, 600	Hydrogen gas charged at 723 K, tested at room temperature
K500	Cathodic charge, seawater

hydrogen. Hydrogen may be supplied by a number of sources, including water vapor, pickling acids, and hydrocarbons. The amount of absorption depends primarily on the titanium oxide film on the metal surface, and an adherent unbroken film can significantly retard hydrogen absorption.

Titanium and its alloys become embrittled by hydrogen at concentrations that produce a hydride phase in the matrix. The exact level of hydrogen at which a separate hydride phase is formed depends on the composition of the alloy and the previous metallurgical history. In commercial unalloyed material, this hydride phase is normally found at levels of 150 ppm of hydrogen; however, hydride formation has been observed at levels as low as 40 or 50 ppm of hydrogen. Figure 10 is an example of hydrided titanium.

At temperatures near the boiling point of water, the diffusion rate of hydrogen into the metal is relatively slow, and the thickness of the layer of titanium hydride formed on the surface rarely exceeds approximately 0.4 mm (0.015 in.), because spalling takes place when the hydride layer reaches thicknesses in this range.

Hydride particles form much more rapidly at temperatures above approximately 250 °C (480 °F), because of the decrease in hydrogen solubility within the titanium lattice. Under these conditions, surface spalling does not occur, and the formation of hydride particles through the entire thickness of the metal results in complete embrittlement and high susceptibility to failure. This type of embrittlement is often seen in material that has absorbed excess hydrogen at elevated temperatures, such as during heat treatment or welding, and subsequently has formed hydride particles during cooling.

There have been instances of localized formation of hydrides in environments where titanium has otherwise given good performance. Investigations of such instances suggest that the localized formation of hydrides is the result

Fig. 10 Severely hydrided unalloyed titanium

of impurities in the metal (particularly the iron content) and the amount of surface contamination introduced during fabrication.

There is a strong link between surface-iron contamination and formation of hydrides of titanium. Severe hydride formation has been noted in high-pressure dry gaseous hydrogen around particles of iron present on the surface. Anodizing in a 10% ammonium sulfate solution removes surface contamination and leads to thickening of the normal oxide film.

In chemical-plant service, where temperatures are such that hydrogen can diffuse into the metal if the protective oxide film is destroyed, severe embrittlement may occur. For example, in highly reducing acids where the titanium oxide film is unstable, hydrides can form rapidly. Hydrogen pickup has also been noted under high-velocity conditions where the protective film erodes away as rapidly as it forms.

Hydrogen contents of 100 to 200 ppm may cause severe losses in tensile ductility and notched tensile strength in titanium alloys and may cause brittle delayed failure under sustained loading conditions. The sensitivity to hydrogen embrittlement from formation of hydrides varies with alloy composition and is reduced substantially by alloying with aluminum.

Care should be taken to minimize hydrogen pickup during fabrication. Welding operations generally require inert gas shielding to minimize hydrogen pickup. Hydrogen can be removed from titanium by annealing in vacuum.

Transition and Refractory Metals

Tantalum, zirconium, uranium, thorium, and alloys of these metals, when exposed to hydrogen, can sustain severe damage due to hydride formation.

Tantalum absorbs hydrogen at temperatures above 250 °C (480 °F), resulting in the formation of tantalum hydride. Hydrogen absorption also can occur if tantalum is coupled to a more active metal in a galvanic cell, particularly in hydrochloric acid. As little as 100 ppm of hydrogen in tantalum cause severe embrittlement by hydride formation.

Zirconium and its alloys are highly susceptible to embrittlement by hydride formation. Absorption of gaseous hydrogen into zirconium and its reaction with zirconium to produce the hydride ZrH_2 occur at an extremely fast rate at 800 °C (1470 °F). This hydride is very brittle, and it may be crushed into a powder. The hydrogen may then be pumped off, leaving a powder of metallic zirconium.

Zirconium alloys can pick up substantial amounts of hydrogen during exposure to high-pressure steam. Zirconium with 2.5% Nb corrodes in water at 300 °C (570 °F) at a rate of approximately 25 μm per year and picks up hydrogen at the rate of 2 to 4 mg/cm^2 (13 to 26 mg/in.^{2}) per day. Hydrogen can be removed from zirconium and its alloys by vacuum annealing.

Uranium, uranium alloys, and thorium are susceptible to hydrogen embrittlement.

Hydrides in thorium have been identified as ThH_2 and Th_4H_{15}. The hydride in uranium is UH_3. Uranium absorbs hydrogen from three sources: fused salt bath annealing, etching and electroplating operations, and corrosion. A hydrogen pickup of 1 to 2 ppm as a result of salt bath annealing noticeably reduces elongation. Hydrogen absorbed during etching and electroplating is concentrated at the surface and does not degrade tensile properties. Corrosion of uranium in water or water vapor reduces tensile ductility. Uranium is embrittled in water over the pH range of 5 to 10.

Analysis of Hydrogen Embrittlement in Commodity-Grade Steels

Hydrogen embrittlement refers to the degradation of mechanical properties due to the presence of dissolved atomic hydrogen, and it often results in ambient-temperature and delayed cracking of steel parts that have recently been assembled. Because of the wide economic impact in commodity-grade components and the frequent difficulty in diagnosing hydrogen embrittlement failures, this section discusses preservice and early-service fractures of commodity-grade steel components suspected of hydrogen embrittlement. Preservice and early-service failures of commodity steels strongly suggest the delayed nature of hydrogen embrittlement, but in many cases, it may difficult to conclusively confirm hydrogen as the root cause; other factors besides hydrogen may be contributing.

The sources of the difficulty in analyzing parts that are suspected of hydrogen embrittlement failure are many. One reason is because the effects of hydrogen embrittlement can be quite varied. In many cases, the loss of strength due to the presence of hydrogen is only one of many factors that allow an unexpected fracture. In other cases, the loss of strength is spectacular, leaving only 10% of the expected tensile strength compared to a nonembrittled component. However, even in these severe cases, it may be difficult to prove with any degree of certainty that the most significant cause of the fracture was the presence of hydrogen.

When the compromised mechanical properties in the subject part(s) are due to hydrogen embrittlement, there may be a tendency to focus on the reduction of hydrogen as a solution. In fact, the hydrogen concentration is only one of many factors that combine to create a realistic picture of "the physical root cause" of the unexpected hydrogen embrittlement fracture.

Preservice and Early-Service Failures

Hydrogen embrittlement can be a likely potential problem in preservice and early-service fractures of commodity-grade steel

components. In certain applications, where steels are processed so that their yield strength is a high percentage of their tensile strength (such as springs, spring clips, and externally threaded high-strength or self-tapping fasteners), hydrogen embrittlement can cause a lot of consequential economic damage. This is especially a problem when the cracks are found after assembly, and labor and other components of the assembly must be scrapped along with the cracked parts. Parts with very hard surface layers, intentionally produced by carburizing or carbonitriding, also increase the likelihood of hydrogen embrittlement problems.

People employed in industries that use high volumes of small components also are sometimes faced with the prospect of creating lot-containment plans when only a few of a large batch of components were diagnosed with hydrogen embrittlement. This happens when any further failure is unacceptable for either safety or economic reasons. Significant expenditures for prevention of hydrogen embrittlement may be worthwhile economically if the damage of the often-inexpensive embrittled components causes a more complex and costly assembly to be scrapped.

Hydrogen embrittlement problems are detected during shipping, inspection, and shortly after placement in service. If the part broke when it was subject to an impact condition, it would not usually be considered a hydrogen embrittlement problem, although it is possible that a preexisting hydrogen embrittlement condition allowed the impact event to separate the fragments more easily. This small example illustrates the difficulty encountered by anyone who tries to make up a simplified testing and data-interpretation guideline for any type of failure.

In these types of situations, the first step is to review the history of the failed part(s) and determine if conditions necessary for delayed hydrogen-induced cracking may be present. Hydrogen embrittlement in steels is most prevalent in components that:

- Have been in contact with atomic hydrogen at some time during their processing
- Are subject to sustained tensile stresses (applied and/or residual)
- Have high hardness from strengthening by heat treatment, cold working, or surface treatment

Other major factors include the hardness range specified and the consistency of actual hardness values; design stress level and actual stress consistency; dimensional consistency; composition, including intentional alloying elements and residuals; and microstructure. The significance of dimensional consistency should not be overlooked, because in some designs, small changes in dimensions can be associated with large changes in localized stress levels.

These factors are briefly reviewed in more detail in the following sections, followed by discussions on the factors that may influence the threshold of delayed HSC.

Hydrogen Sources

Many small commodity-grade components are produced with various secondary manufacturing operations that provide ready sources for the atomic form of hydrogen. The most common causes are toward the top of the list:

- Electroplating
- Acid cleaning
- Phosphate conversion coating
- Caustic cleaning
- Heat treating where hydrogen is used as a protective atmosphere and parts are not tempered after exposure
- Moisture pickup during melting and refining of molten steel

Although caustic cleaning has been associated with embrittlement of steels, electroplating processes can be particularly damaging, because many of the baths produce heavy concentrations of atomic hydrogen at the interface of the base material and plated layer. While the hydrogen atoms can diffuse readily into the iron matrix of the steel, the zinc or cadmium plating acts as a barrier to any hydrogen atoms that may have otherwise randomly diffused away from the structural portion of the component. This creates a situation where hydrogen builds up in the steel.

The chemical reaction that creates the hydrogen during acid cleaning may be very similar to that which corrodes the base metal in SCC. However, the focus here is on pre- or early-service failures. Of course, many corrosion processes can generate hydrogen that can cause embrittlement, but pre- or early-service failures are obviously limited to the context of hydrogen charging during processing of the part. If the local hydrogen concentration and stress-level combination is more than the material can resist (over the threshold level), the crack starts to grow. However, the distinction between hydrogen embrittlement and stress corrosion still should be considered carefully in preservice situations. For example, evidence of hydrogen embrittlement due to an excessive time in the acid cleaning bath should be described as hydrogen embrittlement from the manufacturing process. However, evidence of hydrogen embrittlement due to corrosion of the assemblies that sat on a shipping dock unprotected from ice-melting salt may more correctly be described as SCC.

Sustained Tensile Stresses

Sustained tensile stresses are more likely to cause hydrogen-embrittlement-related cracking, because tensile stresses actually change the shape of the interatomic spaces. This makes it easier for the hydrogen atom to "fit" in. Thus, there is a synergistic effect for the efficiency with which hydrogen atoms cause embrittlement. The regions of a part that have high tensile stress are more likely to crack, not just because many cracks initiate in the presence of a tensile stress, but the tensile stress itself causes the hydrogen atoms to diffuse toward the areas of highest tensile stress. Grain boundaries stressed in tension seem to be a particularly attractive location for the hydrogen atoms. The actual manner in which the presence of the hydrogen in the high-tensile-stress grain boundaries reduces the material strength or otherwise embrittles the material is not entirely known or necessarily explained by one mechanism, such as the decohesive theory previously noted (Ref 1, 2).

Many people who are involved for the first time in a hydrogen embrittlement problem may wonder why there is a sustained tensile stress before the part is put into service. In this regard, residual stresses from heat treating or assembly stresses are often much higher than most people realize and can produce residual tensile stresses in components. Thus, a practical understanding of residual stresses is important, along with techniques in the measurement of residual stresses (e.g., see "X-Ray Diffraction Residual-Stress Measurement in Failure Analysis" in this Volume, or the article "Residual-Stress Measurements" in *Mechanical Testing and Evaluation*, Volume 8 of *ASM Handbook*, 2000).

As an example of a part with a sustained tensile stress due to assembly, consider externally threaded fasteners. When a bolt is threaded through holes in two pieces of sheet metal, it must be tightened to hold the components securely in place. While most threaded fastener installation specifications still call out a minimum torque, it is the tensile clamping stress that actually provides the fastening effect. Thus, the whole body of the fastener between the underside of the head and the nut is in tension before the whole assembly is ever placed into service. Normally occurring stress-concentration factors mean that the highest stress is at the root of the external thread. Because cracks can initiate wherever the local stress exceeds the local strength, thread roots are an area that has a higher chance than the surrounding material to initiate a crack. Again, the presence of the hydrogen allows cracking to occur at stress levels much lower than those required to propagate a crack in the absence of the hydrogen.

As another example, consider a U-shaped spring clip that is inserted into a notch in a plastic molded part. In order for the clip to stay in place during its service life, the assembly is designed so that the clip is held in a position that is slightly pinched closed and from which it "wants" to spring back open. This configuration creates a tensile stress at the outer surface of the U-portion of the clip. The presence of any tool marks or scratches can increase the local stress level to an even greater degree.

Factors Affecting Delayed Hydrogen Stress Cracking

As previously noted in the section "Internal Reversible Hydrogen Embrittlement" in this article, there is a particular value of the stress or threshold that causes a particular component to crack due to hydrogen embrittlement. This threshold is dependent on a number of factors, including:

- The nominal strength of the nonembrittled part
- The amount of hydrogen present in the steel
- The location of the hydrogen in the microstructure
- The presence of other embrittling elements or microstructural phases

The latter item is particularly important, because other embrittling elements or phases in the grain boundaries can cause intergranular fracture or assist hydrogen concentration in the grain boundaries. It should also be noted that hydrogen embrittlement may be present in a component without causing a crack. If the combined levels of stress, hydrogen concentration, and susceptibility are not present, evidence of the embrittlement may not appear.

Nominal Strength of the Nonembrittled Part

While higher-strength parts have less ability to deform in general, the effect of hydrogen is strongly nonlinear in this respect. Many older references (1970s and 1980s) use 40 HRC or tensile strength of 1240 MPa (180 ksi) as the lower susceptibility limit for hydrogen embrittlement. This is an important point, because components that have a local equivalent hardness value of 45 HRC may lose up to 90% of the strength value that they would have without the hydrogen. This shows that a lower hardness and thus lower-strength part (by standard static load test rating systems) may perform when a higher-strength part fractures. Design engineers who are not familiar with hydrogen embrittlement often have trouble understanding that the way to prevent recurrence of the fracture is to lower the specified strength. While components of much lower strength levels than 40 HRC have also been found to have hydrogen embrittlement, these situations are less common.

The residual-stress levels required to produce hydrogen embrittlement in steels of hardness values in the Rockwell B range are very high and are uncommon even after reasonably severe forming operations. Heat treated medium-carbon steels seem to have a greatly increased susceptibility to hydrogen-embrittlement-related cracks when their hardness level is above 43 HRC. Differences in purity levels and other microstructure features, as well as production volumes, may affect both the susceptibility of the steels to hydrogen embrittlement and the analyst's ability to detect that susceptibility due to the presence of actual cracks.

Amount of Hydrogen Present in the Steel

As more hydrogen is present, the embrittling effect increases. Some materials exhibit a threshold combination of stress and hydrogen concentration. Below this value, there is no danger of hydrogen embrittlement cracking (Ref 13). Because most industrial processes for high-volume parts have significant variations in actual processing conditions, it may be extremely difficult to know what the actual range of hydrogen concentration is. It is obviously even more difficult to know which particular part had the most damaging combination of stress, hardness, and hydrogen concentration. Also, note that the type of hydrogen that causes the classical delayed HSC is atomic or "nascent" hydrogen, while the formation of molecular (H_2) hydrogen gas in steels or metals is a different type of hydrogen damage.

Location of the Hydrogen in the Microstructure

In general, the hydrogen is most damaging when it is in the grain boundaries. To compound this effect, the grain boundaries are often the most comfortable and accessible position for the hydrogen atoms, especially those that enter the steel through cleaning or plating processes or heat treating operations. Hydrogen atoms also tend to migrate and reside at many nonmetallic inclusion boundaries (boundaries of internal "impurities" such as sulfides or oxides) or at imperfections (dislocations) in a crystal lattice. It has been well known for decades that proper postplating baking of electroplated parts can minimize the occurrences of cracking due to hydrogen embrittlement. For many years, people thought that the hydrogen was removed from the steel by the baking process, and many older references state that baking removes the hydrogen. In fact, the currently accepted theory explains that the mild heat exposure recommended for postplating baking (generally, approximately 200 to 300 °C, or 390 to 570 °F) gives the hydrogen atoms that are concentrated in the grain boundaries enough thermal energy to diffuse to nonmetallic inclusion boundaries or dislocations, so-called "deep traps." It is much more difficult for the hydrogen to assist in crack propagation when it is in these deep-trap positions.

Presence of Other Embrittling Elements or Microstructural Phases

The fact is that it is often very difficult, especially within the budget and time allowed for many investigations, to determine with certainty whether other embrittlement phenomena have contributed to the brittle condition under investigation. Antimony, phosphorus, tin, sulfur, lead, and other low-melting-point impurities, which are generally very expensive to analyze, may be contributing to the embrittlement situation. These elements come from the raw steel and, similar to hydrogen, are more damaging when they are present in the grain boundaries.

As with hydrogen, it is very difficult to find these other elements at the grain boundaries that they are supposedly embrittling, because they are generally present in very small amounts. The energy-dispersive x-ray spectroscopy (EDS) unit of a scanning electron microscope that is so useful for many failure analysis projects is useless for this analysis, because the layers of antimony, tin, and so on are so thin that they are not detectable with an EDS. They would often be detectable with an Auger spectrograph, if one had very clean (pristine) specimens. However, for many projects for small, inexpensive commodity components, it is difficult to convince the parties who have suffered the loss to invest in an Auger analysis, even if a clean-enough part is obtained.

Thermal exposures can also cause intergranular fracture, such as the well-known temper embrittlement of low-alloy steels. Some of the extended baking times that have been recommended for hydrogen embrittlement prevention in electroplated parts may actually increase the concentration of these other low-strength elements in the grain boundaries, even though the temperature ranges suggested are different from those that are said to cause temper embrittlement.

Diagnosing Hydrogen Embrittlement

While the damaging effects of hydrogen on many metals have been well documented for decades, proving that components have been subject to hydrogen embrittlement can still be very challenging. Some of the reasons include the synergistic nature of hydrogen embrittlement with stress and grain-boundary conditions. If the microstructure has a noticeable second phase in the grain boundaries, the experienced and competent analyst refrains from giving a high-certainty diagnosis of hydrogen embrittlement. The effects of hydrogen embrittlement also can be varied, and many other damage mechanisms can cause fracture appearances that are very similar to those displayed by hydrogen embrittlement.

Another difficulty is the detection of hydrogen as proof, because detecting the miniscule concentrations of hydrogen that could cause the loss of strength is difficult and costly. Analysis of the amount of hydrogen present in a part at the time of the fracture is also virtually impossible, because the hydrogen that facilitated the crack usually evaporates from the fracture surface shortly after the crack opens. Moreover, bulk hydrogen analysis often sheds little light on the concentrations of hydrogen present in the thin layers of material adjacent to what became the crack surfaces.

Other reasons may be more closely related to budgetary constraints than technical limitations. Preservice and early-service failures of

commodity steels may strongly suggest hydrogen embrittlement, but budgets may not allow for extensive analysis (depending on the extent of failure). The financial resources available to perform a failure analysis in such cases are often limited, if nobody was injured. In contrast, SCC (where parts are frequently components of costly equipment and often cause expensive, unplanned shutdowns) may require funds for a more comprehensive analysis.

In any case, it is often less important to be certain that the root cause was hydrogen embrittlement than it is to become aware of underlying contributors, such as high hardness or good design to minimize localized tensile stresses in the components. Despite the difficulties in coming to a certain conclusion in a given situation, it is usually not very difficult to determine whether hydrogen embrittlement may have been a major contributing factor in a particular fracture. The following guidelines are given to help plan a failure analysis that is geared to find out whether hydrogen embrittlement was a likely significant factor in an unexpected fracture. Properly performing this analysis may help to diagnose what the problem is, whether or not hydrogen embrittlement is involved (Ref 14).

Streamlining the analysis process does not imply that relevant tests may be left out or that a competent analyst does not have to collect background data and review the data before conclusions are drawn. The purpose of this section is to help make the best use of the failure analysis resources. People involved in failure analysis are often asked if they can do a hydrogen embrittlement test. What this often means is, "Can you do a fracture analysis and determine whether the fracture was due to hydrogen embrittlement?" Of course, it also sometimes means, "Can you test my as-manufactured parts to find out if they are free from the combination of factors that may cause hydrogen embrittlement?" Many other meanings are also possible. It behooves all concerned to clarify the meaning of the question prior to proceeding with the investigation.

General Questions to Consider on the Possibility of Hydrogen Embrittlement

Characteristics that should be considered in evaluating the possibility of hydrogen embrittlement include:

- *Is the subject component broken?* An intact part may be embrittled and just not broken yet. It is difficult to give a certain answer that an intact part is free of embrittling factors, unless a sustained-load test is conducted to see if the part breaks. A broken part provides a fracture path to characterize. Intergranular fracture at the initiation site is another potential indicator of hydrogen embrittlement.
- *Was the part deformed noticeably before or during the cracking?* Embrittlement means that the part broke in a macrobrittle manner

and has more or less the same shape after the fracture that it had before, except for the extra surfaces.
- *Has the subject component been in service for more than a week?* Most hydrogen embrittlement happens during assembly or relatively soon after being placed in service. Once something is in service, even if it turns out to be hydrogen embrittlement, there are other questions regarding service conditions that should be included in the investigation, and a more comprehensive and open-structured investigation is called for than the streamlined protocol suggested here.
- *Has the part been electroplated or coated with iron or zinc phosphate?* Electroplating and phosphating can often cause high concentrations of atomic or nascent hydrogen to diffuse into the material. This is a known source of hydrogen.
- *Has the part been acid cleaned?* The acid reacts with the iron and creates atomic hydrogen at the part surface.
- *Does the part have a hardness value over 40 HRC?* Higher-hardness parts are more susceptible to hydrogen embrittlement.
- *Did the part break due to a sudden impact load?* It takes time for the hydrogen to diffuse to the final crack path. Of course, it is possible that the part was already cracked due to fabrication stresses, but nobody noticed until a sudden load was applied. The microfractographic features are different in this case from a part that fractured entirely due to hydrogen embrittlement.
- *Has the part been heavily cold worked?* Heavy cold work, especially in parts that are not subsequently stress relieved, can create residual-stress levels that are very near the yield strength of the material. This is an ideal situation for hydrogen-assisted cracks to propagate.

Minimum Test Plan

Even if all the answers to an initial set of questions point to the probability of hydrogen embrittlement being the damage mechanism, other questions must be answered prior to coming to a valid conclusion, and other questions must be answered if an appropriate prevention strategy is desired. These other questions usually require testing. A minimum test plan for a suspected hydrogen-embrittled component follows. The analyst must keep in mind that many other damage mechanisms cause fracture appearances that are very similar to those displayed by hydrogen embrittlement.

Moreover, it is also important to reiterate that hydrogen embrittlement can be manifested in various forms. Less-severe hydrogen embrittlement cracks may even grow by microvoid coalescence, rather than the intergranular cracking typical of high-strength steels. However, most of the hydrogen embrittlement cracks that initiate failure analysis

projects do have some intergranular crack growth near the initiation site that grows under a sustained, static stress. In the more subtle mechanical-property degradation cases, the hydrogen causes a significant reduction in ductility, especially during a slow strain-rate load test.

Visual Examination for Fracture-Surface Orientation

The goal is to determine the orientation of the stresses that caused the fracture. Are these stresses in line with what was expected from the loading that was applied? Is there a reason that there would be high residual stresses that could create the crack geometry?

Visual Examination or Optical or Electron Microscopy

Visual examination, if possible, on larger parts or optical or electron microscopy on smaller parts is used to determine the crack-initiation site. For small clips and threaded fasteners, the fracture surface often looks the same everywhere, so stress analysis principles are required to obtain an idea of where the origin may be. For example, as previously noted, in an externally threaded fastener, the initiation is usually at or near the thread root. If the crack does not travel through the thread root, it is likely that a manufacturing imperfection, such as a thread rolling lap, is present. This does not mean that the damage mechanism was not hydrogen-assisted cracking. However, if the goal is to determine "why this part cracked," it is possible that the lap was an important factor that allowed the crack to propagate.

Visual examination should also include focusing in on the general appearance, color changes, nicks, gouges, machining marks, other damage, and so on. Any such features should be studied and thought about in order to form a reasoned explanation of whether they may be indicative of a factor that contributed to the fracture. Even if the reasoning is incorrect, taking the time to formulate a line of reasoning increases the chances of a proper analysis.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) can be used to determine the crack path with respect to the microstructure, especially at the initiation site. Classical hydrogen embrittlement generally creates intergranular cracks, especially in the area near crack initiation. However, as already mentioned, hydrogen can also have other effects that limit ductility on a macroscale but still allow some microductility. The presence of very small ductile dimples on grain-boundary facets can be confusing to the beginning practitioner. It is important not to go to a high magnification before examining the part at lower magnifications. In plated parts, the crack may be intergranular at the initiation site and all around the edge of the fracture surface adjacent to the plated surface layers. The interior of the

part may have cleavage or ductile dimples showing some microvoid coalescence.

The presence of plating on the crack surface, easily detectable, in general, with the EDS microchemical analysis feature of an SEM, can indicate that a crack was present prior to the plating operation. If the crack path under the plating is intergranular, it could have been hydrogen-assisted cracking due to hydrogen in the raw material or from a heat treating operation; however, this is rather unusual in most modern steelmaking and proper heat treating operations. Quench cracks are often intergranular and usually happen before the part goes through the plating operation. This may allow plating to be deposited on the crack surface.

Some of these problems are difficult to sort out without spending quite a bit of time doing careful, thoughtful lab work. Sometimes, it is impossible to distinguish hydrogen embrittlement from other forms of embrittlement.

Optical Metallography

Optical metallography must be performed to determine whether there are any microstructural conditions that may be contributing to intergranular fracture, if the part does show intergranular fracture. For example, if the part is full of retained austenite or intergranular carbides, that may be a bigger problem than any hydrogen in the part. If the microstructure has a noticeable second phase at the grain boundaries, the experienced and competent analyst refrains from giving a high-certainty diagnosis of hydrogen embrittlement. This emphasizes the importance of a good, general materials background for the failure analyst.

Recommendations on Prevention of Hydrogen Embrittlement

The final stage of an effective investigation is the process of making recommendations to prevent future failures. In fractures suspected of hydrogen embrittlement, recommendations on prevention and remedial action can be most important. Rather than concentrating on trying to prove the exact metallurgical factors that allowed the crack to happen, the project budget may be more effectively spent on educating those involved in the more practical aspects of prevention.

One of the features of hydrogen embrittlement that often tips the balance in favor of additional expenditures for prevention is the fact that, for many applications, the fractures that result from the embrittlement do not happen until several hours or days have passed since the part was assembled. Suppliers of subassemblies are often subject to heavy financial penalties if they supply parts that are obviously defective. There have been many cases where the embrittled parts looked perfectly normal after assembly yet arrived in a cracked condition after a day or two. In industries that subscribe to the just-in-time delivery philosophy, unexpected delays due to broken parts and the associated sorting and part shortage problems can obviously be perceived to be a cause of economic damage.

Guidelines for preventing hydrogen embrittlement are.

Specify a Proper and Appropriate Hardness Range

To minimize the chance of hydrogen embrittlement, reduce the hardness. Never specify a hardness range on a quench-hardened steel part that cannot be obtained on the alloy in question after effective tempering. While hydrogen embrittlement has been documented in steels as soft as 85 HRB, problems increase in frequency when the specified equivalent hardness range includes values as high as 40 HRC. While much of the literature reports results based on tensile strength values, it is often more practical to speak in terms of hardness levels. Aside from the fact that many of the parts that are subject to hydrogen embrittlement are too small to provide a tensile test coupon, the most susceptible parts are those that have a carburized or carbonitrided case. Even one layer of grains at the surface of the part may allow the part to become affected by hydrogen embrittlement. In this case, even the Rockwell hardness test is invalid. The actual test must be performed on a metallographic cross section, using an appropriate-load Knoop or Vickers microindentation hardness test.

Specify Proper Heat Treating and Tempering

To minimize the chance of hydrogen embrittlement, always temper the parts after hardening heat treatments, or anneal or perform a thermal stress relief after severe cold forming. Residual stresses from hardening and cold forming are key factors that could allow the crack to propagate. Stress relief or tempering minimizes the residual-stress level. Lower stress levels equate to higher tolerable levels of residual hydrogen from plating or cleaning operations or even from the raw-steel manufacturing operation.

Ensure Good Cleaning Solution Maintenance

Proper maintenance of acid concentration, temperature, time in the bath, uniformity of any special or proprietary bath additives, as well as proper racking or tumbling to allow draining and rinsing after the cleaning help to minimize the chances of hydrogen embrittlement problems.

Ensure Good Plating Solution Maintenance and/or Proper Selection of Plating Bath Composition

Some plating solutions inherently generate more hydrogen than others. Specifying a low-hydrogen plating process may provide some protection, although an extensive dialogue between the plating chemist and the part specifier may be required to provide significant protection. Proper and frequent maintenance of bath composition and temperature is also very important.

Ensure Proper Postplating Baking Procedure

Most zinc and cadmium electroplating operations have an oven of some sort (batch or continuous) to bake the parts after they are plated. Baking within 1 h of plating has been shown to be very effective at minimizing the danger of hydrogen embrittlement. Delaying the baking cycle beyond 1 h after the parts exit the plating line, such as at shift-change time or when an employee forgets to bake the parts for a few hours or a few shifts, has been repeatedly shown to reduce the effectiveness of the baking. While the causes of this loss of effectiveness are not well understood, anyone using or manufacturing hardened or cold-formed electroplated parts can avail themselves of the knowledge gained from experience.

A more difficult problem sometimes arises with the use of phosphate coatings. Iron phosphate and zinc phosphate corrosion-resistant coatings work by a combination of sacrificial (galvanic) action and oil barrier layer held between the open lattice of phosphate crystals on the steel part surface. The microcrystalline structure of the phosphate is very delicate and can be easily damaged by the conveyor systems commonly used in the coating process lines. Most phosphate lines go directly from the phosphating operation to the oil-impregnation step, because the platers have found that the parts may not meet the commonly specified salt-spray-resistance requirements if they are detoured to a baking operation first. However, some platers have solved this problem. While zinc and iron phosphate are generally less expensive than zinc plating, the design engineer must consider the possibility that postcorrosion prevention-coating application baking is more readily available for plating than for phosphates. Both plating and phosphate coating can allow damaging amounts of hydrogen to diffuse into the steel.

Follow Good Manufacturing Practices

Following good manufacturing practices, in general, including minimization of surface imperfections, appropriate maintenance of forming, heat treating, and plating line equipment, and so on, goes a long way toward minimizing the chances of a given lot of parts experiencing hydrogen embrittlement. One example that is worth mentioning is laps in threads of externally threaded fasteners. Not only can laps reduce the effective load-bearing cross section, but they can entrap acid cleaning solution and plating solutions. If the parts cannot be completely dried, they can start to corrode in these hidden locations. This is an example where the boundary between hydrogen embrittlement and stress corrosion could become very indistinct.

Perform Destructive Testing on Samples

Perform destructive testing on samples from each production lot to minimize the chances of highly embrittled components going into service. ASTM International committees have agreed on protocols for destructive tests of plated steel parts that can detect relatively low levels of embrittlement. However, these tests are not very useful where variability is great within lot hardness. They may give a false sense of security if the hardest parts are not in the sample and may cause unnecessary scrap if the service loads are lower than those required by the standard test method. These destructive tests are also quite time-consuming. They may cause shipments to be delayed if results are required prior to shipping, because the tests may take up to a few days to perform. The rising step load is one of the embrittlement-detection protocols that may be used on parts that are not cracked and that have specific requirements for structural integrity.

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