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Hydrogen Embrittlement of Metals

Atomic hydrogen from a variety of sources reduces the ductility of many metals.

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Hydrogen affects the mechanical properties of most structural metals in several different ways; the result is always a limited capability for plastic deformation, frequently accompanied by a loss in strength. Prior to World War II most serious hydrogen embrittlement problems were associated with large steel forgings and, to a lesser extent, with other wrought steel products. Hydrogen embrittlement problems have since multiplied. The dramatic expansion in the use of welded structures during the war was accompanied by a similar increase in the number of failures attributable to hydrogen. In the postwar period the available strength levels of steel have been continuously increased to meet new commercial and military demands. These increases have generated a host of hydrogen problems.

Besides ferrous metals, the requirements of the nuclear and space age in which we live have necessitated the use of a variety of metals that were of only scientific interest a quarter of a century ago. Some of these have attendant hydrogen embrittlement problems more severe than any of those associated with the ferrous metals.

Kinetics has been a major factor in the widespread but elusive hydrogen embrittlement problems that have plagued industry. For example, in iron and steel, hydrogen can enter quickly and easily, diffuse very rapidly at normal temperatures, and, after having caused a failure, diffuse out again, frequently leaving little evidence of its former presence other than the failure itself. Also, a concentration of hydrogen of only a few parts per million suffices to embrittle many metals, making analysis difficult.

Both because of its scope and complexity and because of its commercial importance, the hydrogen embrittlement problem has intrigued investigators from many disciplines. Surface reactions, electrochemistry, thermodynamics, and material properties, to name a few aspects, all play a part. Even though thousands of investigations have been made, many facets of the problem are poorly understood at best.

Examples of Hydrogen Damage

Some examples of the effects of hydrogen alone, without added stress, on the structure and mechanical properties of a range of metals are shown in Figs. 1 through 3. Figure 1 is a photomicrograph of commercial copper that had been heated in hydrogen; the treatment produced a porous, degenerated structure of low strength and ductility. Figure 2 (*1*) shows the wall of a heavy pressure vessel used in the petrochemical industry that has developed large internal blisters and cracks from the action of hydrogen as a result of sulfide corrosion. Figure 3 shows a vanadium wire that literally shattered when it was cathodically charged with hydrogen in an electrolytic cell.

The most common form of hydrogen embrittlement, however, occurs when ferrous metals containing hydrogen are stressed. The amount of plastic deformation such metals can undergo before fracture is markedly reduced by the presence of hydrogen.

Hydrogen Absorption

Hydrogen enters all metals in atomic form, not as molecular hydrogen. Statistically the hydrogen atom, once it is in the metal, loses all or some of its electrons, becoming a small positively charged ion. It diffuses interstitially in most metals at a rate that is much less sensitive to temperature changes than most solid-state diffusion processes are. This relative insensitivity is reflected, for example, in the low activation energy of approximately 3000 calories per mole for lattice diffusion in iron with a body-centered cubic crystal structure at temperatures above 200°C. The overall diffusion rate in iron, moreover, is high even at temperatures in the neighborhood of room temperature, the value of D being in the range 10^{-4} to 10^{-5} square centimeter per second. In most metals the diffusion rate of hydrogen is higher by many orders of magnitude than that of other elements at comparable temperatures. The diffusion rate is substantially lower, and the temperature dependence greater, when iron or an alloy such as a nickel-chromium stainless steel has a crystal structure that is face-centered cubic rather than body-centered cubic.

In general, any process producing atomic hydrogen at a metal surface will induce considerable hydrogen absorption in that metal. Not all the hydrogen atoms released at the surface enter the metal; a large fraction combines or recombines to form bub-

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bles of gaseous molecular hydrogen. The fraction that penetrates may be significantly altered either inadvertently or deliberately by the presence of chemical species that affect the dissociation and recombination of hydrogen at the surface. Because hydrogen absorption takes place through the surface, the rate of rise of the hydrogen concentration in a specific volume of metal is related to the surface-to-volume ratio. Problems of hydrogen embrittlement will, therefore, be more frequent with fine wire and thin sheet, where the surface-to-volume ratio is high. Conversely, metal in these forms will lose any dissolved hydrogen more rapidly on aging.

In general, the driving force for hydrogen diffusion is a gradient in the activity of the hydrogen in solution. Normally this is equivalent to a concentration gradient. As a result of the high mobility of hydrogen in metals, thermal diffusion or diffusion under the action of a temperature gradient may also be significant. For example, when zirconium or an alloy containing hydrogen is exposed to a temperature gradient, the hydrogen redistributes itself to conform to any changes in activity with temperature. Because of the thermodynamics of this system, the hydrogen concentration increases at the cold end until hydride begins to precipitate at the solubility limit. When a continuous source of hydrogen exists on the high-temperature side, hydrogen will be pumped down the temperature gradient by thermal diffusion, producing large quantities of hydride in the cold region. Under certain conditions this phenomenon can cause failure of the zirconium alloy cladding of fuel elements in nuclear reactors that use pressurized water for heat transfer, after long periods of operation. In other metal-hydrogen systems the thermodynamics may cause the hydrogen distribution to be completely different from that of the zirconium-hydrogen system.

Hydrogen Solubility in Metals

The variation in the solubility of hydrogen with changes in pressure, temperature, and the state of a metal is a major factor in the hydrogen embrittlement process. If hydrogen is absorbed from the gas phase at high temperatures, the equilibrium amount dissolved is proportional to the square root of the gas pressure. Thermodynamically this indicates that hydrogen is absorbed by metals in atomic form. However, the temperature dependence of hydrogen solubility in metals, as well as the amount dissolved, differs widely in different metals. Structural metals fall into two major categories—those in which the solution is exothermic and those in which it is endothermic. The former are characterized by a negative heat of solution, with solubility decreasing with increasing temperature at constant pressure. Such metals dissolve large quantities of hydrogen, forming ordered solutions or definite hydrides. Examples of such metals are cerium, lanthanum, titanium, zirconium, hafnium, thorium, vanadium, niobium, tantalum, and palladium. Conversely, in metals such as copper, silver, chromium, molybdenum, tungsten, iron, cobalt, nickel, aluminum, and platinum, equilibrium solubility for hydrogen increases with increasing temperature. In these metals the equilibrium solubility at room temperature is lower by several orders of magnitude than that of metals with exothermic solubility. It is also drastically lower than the solubility at higher temperatures in most of the metals that dissolve hydrogen endothermically. For example, in iron the equilibrium solubility at room temperature is only 3×10^{-6} atom per 100 atoms, while in the solid phase at the melting point it is 4.3×10^{-2} atom per 100 atoms—a ratio of 1 to 14,000! Moreover, the solubility triples on melting. In metals, such as iron, that undergo allotropic transformation with changes in temperature, the solubility, as well as the diffusivity, also depends on the crystal structure. At the temperature of transformation, the high-temperature face-centered cubic allotrope of iron can contain nearly twice as much hydrogen in equilibrium solution as the body-centered cubic form at the same temperature. A number of the problems with hydrogen that occur during the manufacture of iron and steel are a result of these often enormous solubility changes, since all excess hydrogen must be somehow accommodated when the hot metal cools or transforms. Measurements of the hydrogen solubility in ferrous metals at room temperature, however, usually show hydrogen concentrations far in excess of the value given for equilibrium lattice solubility. Thus it appears that a large percentage of the excess hydrogen remaining in the iron or steel after solidification diffuses to pores, cracks, and other lattice imperfections and forms high-pressure molecular hydrogen as the temperature drops.

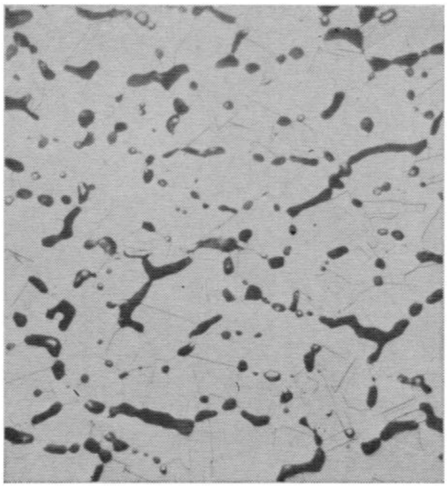


Fig. 1. Structure of commerical copper after heating in hydrogen for 3 hours at 750°C (about × 250).

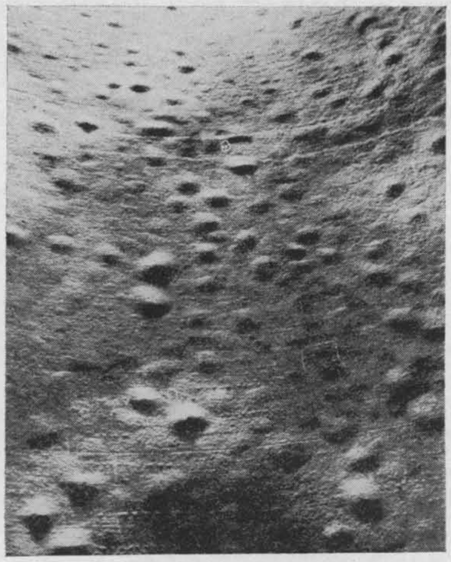
Sources of Hydrogen in Metals

Hydrogen may be absorbed by metals both during processing and when the metals are in use. In the melting and casting of metals the most frequent source of hydrogen is the reaction of the hot metal with moisture contained in the raw materials or in humid atmospheres, to form an oxide and hydrogen. Most molten metals readily absorb large quantities of the hydrogen thus released. Hydrogen absorbed in this manner has, until fairly recently, been a major source of subsequent problems with large steel castings. Now the use of vacuum degassing equipment to remove the hydrogen from the liquid metal at one of several stages in the steelmaking process has reduced this problem to a minimum. In the arc welding of steels, also, atmospheric moisture can be a source of hydrogen; the primary source, however, is undoubtedly the electrode coatings. Both inorganic and organic coatings may be sources of hydrogen, as a result of high-temperature decomposition or liberation of water of hydration.

During at least one stage in the finishing of metal articles, it is usually necessary to clean them chemically or electrochemically, either to improve their appearance or to prepare them for further processing, such as electroplating or painting. The reaction of the metal with the acid used to clean it releases quantities of nascent hydrogen at the metal surface. Most of it combines to form molecular hydrogen that is released in the form of bubbles; the remainder diffuses into the metal. Metals such as titanium or zirconium that exothermally dissolve large quantities of hydrogen are very sensitive to cleaning or pickling operations of this type. Because of the difficulty of removing hydrogen from these metals once it has been absorbed, great care must be taken to keep the formation of hydrogen to a minimum during chemical cleaning; the alternative is use of various kinds of mechanical cleaning techniques.

Electroplating is also an obvious and very important source of hydrogen in finished metal products, since hydrogen, as well as the electroplate, is deposited on the metal cathode. Because electroplating is often the last step in finishing, there is generally small chance that hydrogen will be inadvertently removed by further processing. The problem of embrittlement through plating is further complicated by the low rate of diffusion of hydrogen through most of the metals used as electroplates. This low rate hinders the subsequent removal of hydrogen. Because of the large number of failures that have occurred in certain sensitive metals, particularly high-strength steels, articles made of these metals are frequently baked at some intermediate temperature after plating to hasten the removal of hydrogen before use. Special electroplating techniques have also been devised to keep hydrogen pickup to a minimum. For the most sensitive metals electroplating has been replaced by other techniques, which completely eliminate the absorption of hydrogen during the metal coating process.

In hydrogen gas, for any temperature and pressure of molecular hydrogen there exists an equilibrium concentration of atomic hydrogen. At normal temperatures this concentration is negligible. In the range of temperatures at which metals are heat-treated, however, both the thermodynamics and the kinetics favor the absorption of substantial quantities of atomic hydrogen from the gas phase. Hydrogenous gases are frequently used to prevent oxidation of the metals that are being heat-treated. If hydrogen pickup is a problem, other nonoxidizing atmospheres must be employed.



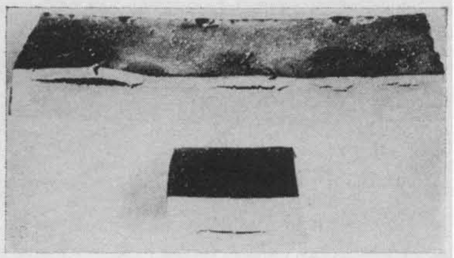


Fig. 2. Hydrogen blisters in the wall of a steel container. (Left) Surface view; (above) cross section. [From Nelson and Effinger (*1*)]

For metals in use, aqueous corrosion is the most common source of hydrogen. During corrosion the metal reacts with water to form an oxide or a hydroxide, with simultaneous release of easily absorbed atomic hydrogen. If the metal is readily embrittled by this hydrogen, the extremely small amounts thus absorbed may cause local cracking and failure. In particular, in nuclear reactors in which pressurized water is used for heat transfer, hydrogen embrittlement of the zirconium alloy fuel cladding, or of the pressure vessel itself, may result from aqueous corrosion. Hydrogen produced by the radiolytic decomposition of the water during operation of the reactor adds to the problem.

Containers of chemicals, used either for storage or as process reaction vessels, are likely to absorb large quantities of hydrogen during long use. Such problems are particularly severe in the petrochemical industry, where the raw materials frequently contain hydrogen sulfide as an impurity. The sulfide ion is particularly deleterious in that it acts as a surface poison, retarding the recombination of atomic hydrogen to form molecular hydrogen at the surface. This promotes absorption of hydrogen by the metal and retards the subsequent evolution of any dissolved gas. Also, the containment of hydrogen or hydrogen-bearing gases under high pressure may cause severe embrittlement problems in the case of certain metals, particularly steels; however, this form of embrittlement, discussed below, may be somewhat different from the normal embrittlement.

Irreversible Embrittlement

The ways in which hydrogen embrittles different metals are nearly as varied as the ways in which these metals come in contact with hydrogen during fabrication or when they are in use. For the sake of completeness in this general discussion, I include all the forms that have been loosely termed "hydrogen embrittlement" in the past, although individuals with a sophisticated understanding of the effects of hydrogen on metals usually refer to only one, and at most two, of these types of embrittlement as hydrogen embrittlement. The effects of hydrogen on the mechanical properties of metals can be loosely classified into two broad categories: irreversible and reversible. I discuss the irreversible types first, but only brief-

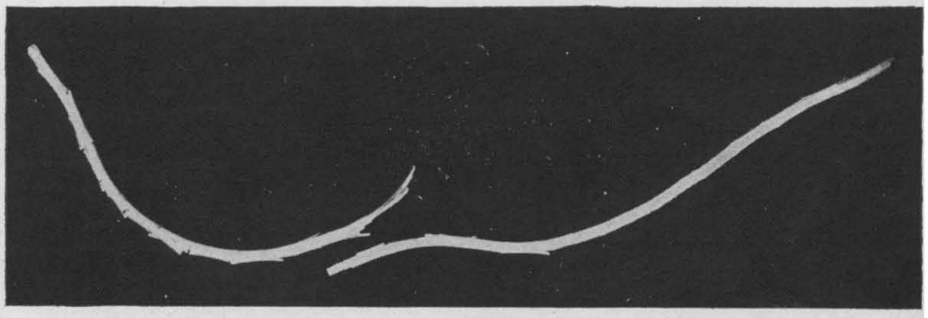


Fig. 3. Vanadium wire shattered by cathodic charging with hydrogen.

ly, concentrating principally on the more complex reversible embrittlement.

In irreversible embrittlement, hydrogen absorption is accompanied by severe damage to the metal structure, damage which degrades its mechanical properties. This damage remains even after all traces of hydrogen have been removed. High temperature is usually a prerequisite for irreversible embrittlement. For example, when commercial copper containing numerous oxide inclusions is heated in hydrogen to temperatures in the neighborhood of 300°C or above, the hydrogen diffuses into the metal and reacts with the inclusions to form water vapor and metallic copper. At high temperatures, sufficient pressure is generated by this vapor to expand the small inclusion sites into relatively large voids in the soft copper, thus producing the weak, porous structure shown in Fig. 1. This form of embrittlement has sometimes been referred to in the copper industry as "hydrogen sickness." High-purity copper behaves differently from commercial tough pitch copper because high-purity copper contains very few oxides with which the hydrogen can react. Consequently, hydrogen has very little effect on its mechanical properties.

Hydrogen Attack

In the chemical and petrochemical industries, a similar type of embrittlement in steel, termed "hydrogen attack," has tremendous economic consequences, as it is a major cause of failure in containers at high temperatures. The strength of steels depends to a large extent on the specific size and distribution of carbides in an iron alloy matrix. When low-alloy steels are exposed to hydrogen at high temperature the dissolved hydrogen reduces the iron carbide, cementite, to metallic iron and methane gas. This causes a form of structural deterioration in the steel somewhat similar to that which occurs in commercial copper. The strengthening carbides tend to disappear, both by the methane reaction and by the diffusion of carbon from unreacted carbides to sites where reaction with hydrogen has locally reduced the carbon activity. This structural alteration and disappearance of carbides, added to the effects of the insoluble methane gas, produces a weak material of relatively low ductility. In industry, where the continued use of low-alloy steels is dictated by economics, steels more resistant to hydrogen attack have been developed. Additions of titanium and vanadium in sufficient quantity to tie up the carbon in the form of carbides stable with respect to hydrogen are very effective. Chromium and molybdenum in larger additions are also effective.

Some ductility can be recovered in these embrittled steels by means of a high-temperature heat treatment. This partial recovery of ductility does not arise from the removal of hydrogen, however, but depends primarily on the thermal rearrangement of the damaged structure. Because substantial quantities of the strength-producing carbides have been removed permanently, the loss in strength is generally not recoverable to any appreciable extent.

Blistering

In addition to these two forms of permanent hydrogen damage occurring at high temperatures, there is a third, more subtle, type that may occur at room temperature. It is particularly significant in high-strength steels or other notch-sensitive metals. The blisters shown in Fig. 2 typify this form of permanent structural damage. Whenever atomic hydrogen is produced at the surface of a metal, some fraction diffuses inward and is retained in solution in the lattice. The concentration of dissolved hydrogen rises, where possible, to a value at which the activity of the dissolved hydrogen equals that of the atomic hydrogen at the metal surface. However, most real metals contain defects of one form or another—such as dislocations, holes, grain boundaries, and interfaces between the matrix and inclusions or second-phase particles—at least some of which act as internal surfaces. Hydrogen in solution can recombine at these surfaces to form gaseous molecular hydrogen. The lattice hydrogen will continue to diffuse to these defects in an attempt to equalize the activity in the gas phase with that in solution. When a large quantity of atomic hydrogen is evolved at the exterior surface, as occurs, for example, during electroplating, the equilibrium concentration of lattice hydrogen is large and the resulting pressure of molecular hydrogen in the defects giving an equal activity is extremely high. Various estimates of this pressure have been made, modified, and remodified. One reasonable estimate is that a concentration of 10 parts per million of lattice hydrogen in iron is in equilibrium with gaseous molecular hydrogen under pressures of 14,000 or more kilograms per square centimeter. Regardless of which calculation is the most nearly correct, evidence exists, in the form of blisters and cracks in ferrous metals, that the pressures are sufficient to enlarge preexisting defects into sites of severe damage. Such damage is not normally reversible without remelting, even though all lattice hydrogen and perhaps some molecular hydrogen is removed. In a metal sensitive to this form of defect—as high-strength steel is at normal temperatures, or perhaps iron or a mild steel is at low temperatures—these blisters and cracks will act as sites for initiating brittle fracture.

The types of hydrogen embrittlement described above are found in impure or two-phase metals. Another form of embrittlement that may appear even in high-purity metals of the group of metals that exothermically dissolve large quantities of hydrogen—for example, zirconium, titanium, vanadium, tantalum, or niobium—depends on hydride formation. Essentially, this type of embrittlement might result from a distribution of any low-strength brittle particles throughout any metal. For hydrogenated metals of this group, the particles are hydrides. Most of these metals have structures sensitive to cracks and stress concentrations. When a stress is applied that is sufficiently high to crack the low-strength brittle hydrides, the notch-sensitive matrix permits these cracks, once initiated, to propagate to failure. Moreover, the hydrides themselves frequently produce additional unfavorable local stresses as a result of the volume changes associated with their formation. These stresses augment the applied stresses and enhance localized cracking of the matrix. Such local stresses alone shattered the cathodically charged vanadium wire shown in Fig. 3.

An important feature of hydride embrittlement in metals is the nature of their sensitivity to rate of strain. Since this sensitivity depends primarily on the inherent tendency of the metal matrix to undergo low-ductility fracture, the embrittling tendency increases as the rate of stressing increases, as in most cracking phenomena at low or moderate temperatures. It is therefore sometimes called impact embrittlement. Limited research on several of these metals has shown that, if the lattice solubility for hydrogen is not exceeded, they may exhibit hydrogen embrittlement of the form I describe below in detail for iron and steel, rather than hydride embrittlement. Besides taking precautions against exposing these metals to sources of hydrogen, one can reduce the tendency toward hydride embrittlement by increasing the lattice solubility for hydrogen. In titanium, for example, this can be accomplished by alloying with aluminum. Reducing the size both of the hydride particles and of the matrix grains by appropriate processing reduces the tendency toward brittleness since it limits the size of the nucleating crack while improving the toughness of the matrix metal.

Reversible Embrittlement

The form of hydrogen embrittlement usually referred to by that name has been examined widely in ferrous alloys, to a moderate extent in titanium alloys, and briefly in some of the less common metals such as vanadium, molybdenum, and niobium. It is the principal form of hydrogen embrittlement in ferrous metals, which as a rule do not form hydrides. This type of hydrogen embrittlement has three identifying characteristics.

1) The ductility (*2*) of a hydrogen-embrittled metal is restored by removal of the hydrogen prior to deformation of the metal—that is, the embrittlement is reversible. The degree of embrittlement (*2*) is related to the hydrogen content over a broad range, as seen in Fig. 4 (*3*).

2) The ductility exhibited by a metal embrittled by hydrogen decreases with a decrease in the rate at which the metal is deformed. This characteristic distinguishes this from other types of brittleness at ordinary temperatures. In hydride-forming metals it has been frequently termed "slow strain rate embrittlement," as contrasted with embrittlement occurring from hydride formation.

3) A temperature range exists in which the ductility of a hydrogen-charged metal reaches a minimum when the metal is deformed at a fixed rate. This range is near room temperature for iron or steel and titanium. Below the minimum the ductility increases with decreasing temperature. Such mechanical behavior in this temperature range is anomalous. For iron and steel, embrittlement of this type apparently disappears above about 175° to 200°C (350° to 400°F). These relationships are illustrated in Fig. 5 (*4*).

Because the overwhelming mass of information has been obtained on iron and steel, further discussion on this form of hydrogen embrittlement centers on these metals.

Delayed Failure

Delayed failure, sometimes called "static fatigue," is the most spectacular facet of this hydrogen embrittlement phenomenon. It typically occurs as a service failure of a part that has been operating for long periods under relatively low stresses without observable deterioration until a major fracture occurs. High-strength steel parts and structures, particularly when electroplated, are most susceptible to this form of embrittlement, although it does occur occasionally in lower-strength steels. Delayed failure is the ultimate extension of the effect of low deformation rates on the enhancement of embrittlement. A hydrogenated metal may be embrittled when subjected to conditions conductive to delayed failure, yet the same hydrogenated metal may exhibit no loss of ductility in a standard tensile test where the strain rate is many times as high. Another aspect of delayed failure is the fact that it may be caused by a transformation or quenching stress as well as by a designed operational stress. Failure under the action of residual stresses gives an air of spontaneity to the failure.

Troiano and his associates at Case Institute of Technology have studied this phenomenon extensively over the past decade (*3, 5, 6*). Figure 4, taken from their work (*3*), shows the effect of metal processing and of the resulting strength level of a steel on the degree of hydrogen embrittlement. They have found similar effects on the susceptibility to delayed failure. Figure 6 (*5*) shows the effects of applied stress and of hydrogen content on the time to failure of notched tensile specimens of a high-strength steel. The shape of these curves typifies the delayed-failure phenomenon. For these experiments the tensile bars were hydrogenated by cathodic charging. The hydrogen content and distribution were then adjusted by means of baking at moderate temperatures. Even after charging, the amount of absorbed hydrogen above the background level of hydrogen was so low as to be undetectable by available analytical techniques. For a given strength level and for different hydrogen contents deduced from differences in baking time, there is a range of stresses over which delayed failure will occur. Within this stress range the time to failure increases with decreasing stress level, although not strongly. At stresses above this range, where the inherent strength of the steel is exceeded, instantaneous failure will occur almost independently of the hydrogen content; below this range, failure does not take place within realistic times. A careful examination of specimens stressed in the laboratory under conditions conducive to delayed failure shows that a brittle crack is in fact growing during the delay period. Final failure takes place when the stress on the uncracked portion of the specimen exceeds the strength of the remaining metal. An incubation period generally follows the application of a stress before a crack is initiated. The effect of hydrogen seems to be reversible during this incubation period.

Spectacular failures have been plane crashes resulting from the delayed failure of high-strength-steel landing gear. Industry in general has been plagued by a multitude of similar hydrogen embrittlement problems in high-strength, high-hardness parts such as springs, lock washers, and high-strength screws or bolts—again, particularly when such parts are electroplated. The considerable time that normally elapses between the time hydrogen is absorbed by the parts at the vendor's and the time the part is stressed and finally fails during use frequently make it difficult to assign the cause of failure to hydrogen. Because so many such failures have occurred in these materials, however, whenever a situation arises similar to those in which hydrogen has been known to cause problems, specifications normally call for practices to minimize the effects of hydrogen. In many cases chemical or electrochemical cleaning is prohibited. Also, protective metallic coatings are frequently applied by means other than electroplating, to assure freedom from hydrogen.

Effects of Structure

The structure and properties of steels are controlled by chemical composition and by the distribution of added elements in the form of solid solutions and second phases, primarily carbides. For a given composition, the strength can be varied over a broad range by heat treatment, through structural changes. The same strength level can often be achieved by two or three different structural paths. Evidence indicates that a steel of a given strength may be susceptible to widely different degrees of hydrogen embrittlement and delayed failure, depending on its structure. When ductility, rather than strength, is considered, evidence shows that the structure in which the carbides are distributed in the form of fine spheroids is the most ductile and the least sensitive to the effects of hydrogen.

Crack Propagation

Recent studies of the effects of environment on the rate of crack propagation in precracked steel specimens have shed light on what may be another effect of hydrogen on steels, possibly related to the more common forms of hydrogen embrittlement. When such precracked specimens are subjected to either monotonic or cyclic stress, as in fatigue, the rate at which the crack propagates is increased manyfold in a dry hydrogen atmosphere relative to the rate in other environments, including an atmosphere of moist hydrogen or hydrogen with an oxygen addition of less than 1 percent. Because small cracks or defects are almost inevitable in commercial structures, this effect may have serious, and as yet widely unappreciated, consequences.

Hydrogen at High Pressures

The effect of hydrogen at high pressures is the aspect of the hydrogen embrittlement phenomenology that I consider last. Many metals become much less ductile when they are stressed in a high-pressure hydrogen environment —that is, in hydrogen at pressures above 100 atmospheres. The embrittlement usually appears to take place very rapidly, but it is substantially reduced if the metal is first exposed to high-pressure hydrogen without stress, then stressed in a hydrogen-free atmosphere. Thus the embrittlement may be merely a manifestation of the environmental effects described above, enhanced by the increased hydrogen pressure. Because the time for hydrogen permeation between exposure of the stressed metal and failure is short, the embrittlement appears to be a surface or surface-layer effect. Containers for hydrogen at high pressure pose a formidable problem, since they are subjected to tensile stresses by the nature of the containment during exposure to the high-pressure hydrogen atmosphere. Vessels that have withstood designed pressures and stresses in tests with other gases frequently cannot contain hydrogenous gases at some fraction of these pressures because of leaks or catastrophic failure. The problem is kept to a minimum by the use of liners of metals, such as the chrome-nickel-stainless steels, through which hydrogen penetrates much more slowly, or by the use of multilayered vessels with vents and weep holes that allow hydrogen to recombine and escape after penetrating the first layer; thus hydrogen is prevented from catastrophically reducing the strength of the entire section.

Mechanism of Reversible Embrittlement

The fundamental nature of the irreversible forms of hydrogen embrittlement, such as hydrogen sickness in copper or hydrogen attack of steel, and the nature of hydride embrittlement are reasonably well understood. Because of engineering need-to-know, much information has also been compiled on the effects of variations in composition, structure, and environmental parameters on reversible hydrogen embrittlement of many metals. The mechanism of this type of embrittlement, however, has intrigued scientists for many years. Its complexity and its interrelationship with surface and diffusion phenomena, structure, and the normal mechanical behavior of metals have made these studies difficult and frequently inconclusive. For example, in a study of the effects of changes in the composition or structure of a metal on the degree of embrittlement by hydrogen, an investigator may *assume*, without resorting to adequate analysis, that test specimens receiving identical exposures to a source of hydrogen absorb the same amount of embrittling hydrogen. Typically this might be during cathodic charging where the electrolyte, current density, and charging time are fixed. If the resulting mechanical behavior of the specimens is not the same, the question is unresolved as to whether the differences arise from a difference in susceptibility to embrittlement or whether the diffusion rate or the surface phenomena have been altered in such a way by the compositional or structural changes that more or less hydrogen has been absorbed by the metal. The difficulty associated with precise hydrogen analyses and the care that must be taken to preserve the hydrogen content that existed during the deformation cause many investigators to take such presumptive shortcuts.

Most metals with body-centered cubic or hexagonal close-packed crystal structures, when stressed, may either deform plastically or fracture by brittle cracking. The transition between the two types of mechanical behavior depends on compositional and environmental conditions. Under specific conditions, if the stresses required for general plastic deformation are lower than those required for the propagation of brittle cracks, then the metal will deform plastically. If the converse is true, brittle fracture will occur. Metals deform plastically through the motion of special linear defects called dislocations. If the number or velocity of moving dislocations should drop substantially during deformation, the stress level must rise if the number or velocity is to be restored to the value needed for continued deformation. This increased stress may then cause brittle fracture locally. In several theories of hydrogen embrittlement it is proposed that hydrogen does in fact interfere with the motion of dislocations and thus promotes embrittlement. Alternatively it has been proposed that hydrogen may lower the stress necessary to cause brittle fracture, possibly by affecting the atomic bonding rather than by affecting the stresses required for plastic deformation. Theories of hydrogen embrittlement generally involve assumptions based on one of these alternatives. In addition, many scientists also invoke the concept that high pressures of molecular hydrogen are generated in defects or cracks—a finer-scale analogy to the large blisters created by hydrogen near the surfaces of metals.

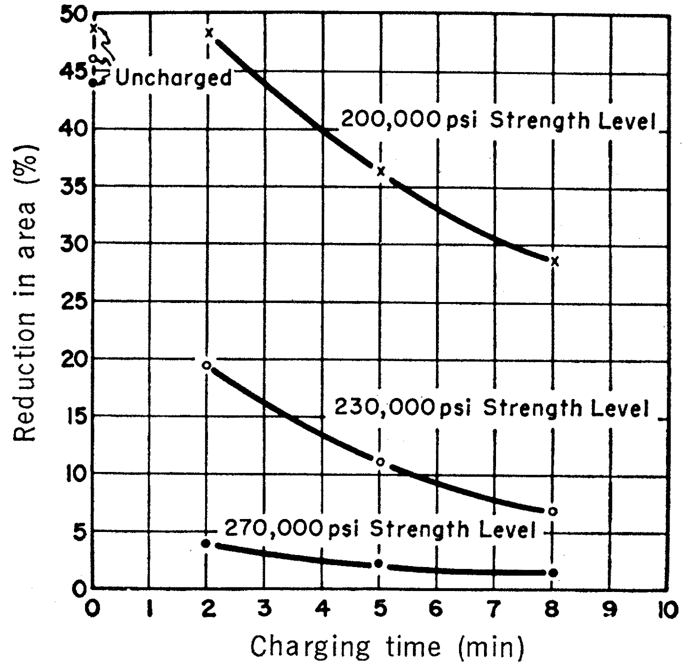
The observed increase in ductility at high strain rates and low temperatures has been generally attributed to a necessity for continued transport of lattice hydrogen to the neighborhood of a moving crack front, this transport kinetically breaking down at high strain rates or low temperatures. Two types of transport have been proposed: interstitial diffusion of single atoms and group diffusive transport of hydrogen atoms accompanying dislocations moving to the region of the crack. My discovery of a low-temperature yield point in hydrogenated iron (*7*) is often cited as evidence of such an attraction between groups of hydrogen atoms and dislocations. This attraction would render the dislocation nearly immobile at low temperatures, while at the higher temperatures, where hydrogen embrittlement occurs, these "atmospheres" of hydrogen atoms would be mobile, accompanying the dislocations as they moved to the region of a growing crack.

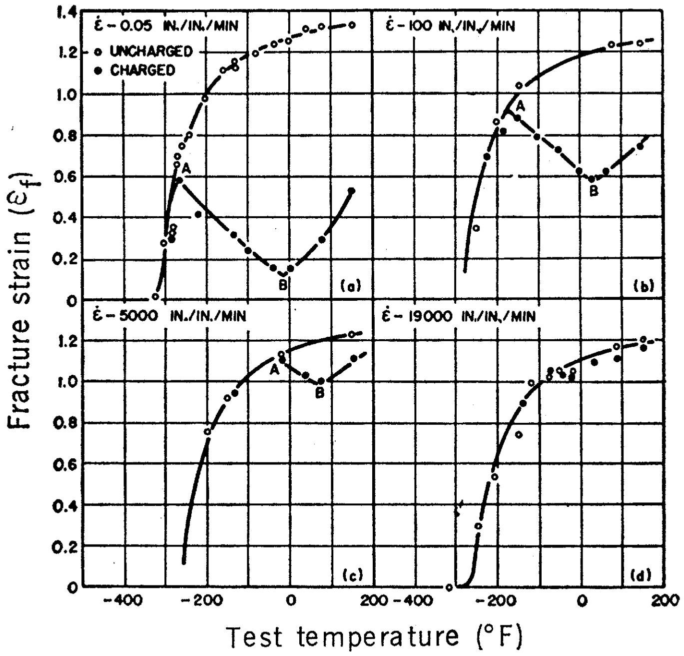
During the early part of this century Griffith (*8*) proposed a now classic model for the size-dependence of fracture in glass filaments. Assuming that flaws of various sizes existed initially, he predicted that such flaws would grow under the action of an applied stress whenever the energy necessary to create additional crack surface was exceeded by the elastic distortion energy recovered by relaxation of the solid surrounding the cracked region. The Griffith relation between the stress σ, the elastic modulus E, the length L, and the energy associated with increasing the crack surface γ, was of the form

$$\sigma \propto \sqrt{\frac{E\gamma}{L}}$$

In glass, γ is merely the classical surface energy. In materials that deform plastically, the energy of plastic deformation associated with crack propagation is a major contributor to this surface term. Petch and Stables (*9*) first proposed that the principal effect of hydrogen in promoting the brittle behavior of ferrous metals was to decrease the surface energy, thus allowing crack growth at lower stresses. Recent results on enhanced crack growth in hydrogen environments at atmospheric pressure lend support to this general argument. It remains a difficult argument to support in detail, however, because the energy of plastic deformation associated with the crack extension in these metals is so much larger than the true surface energy.

Bastien (*10*) is a strong proponent of the dislocation interference model. Tetelman (*11*) has shown that microcracks can be produced simply by cathodically charging an iron-silicon alloy. He proposed, in a modified Grif-





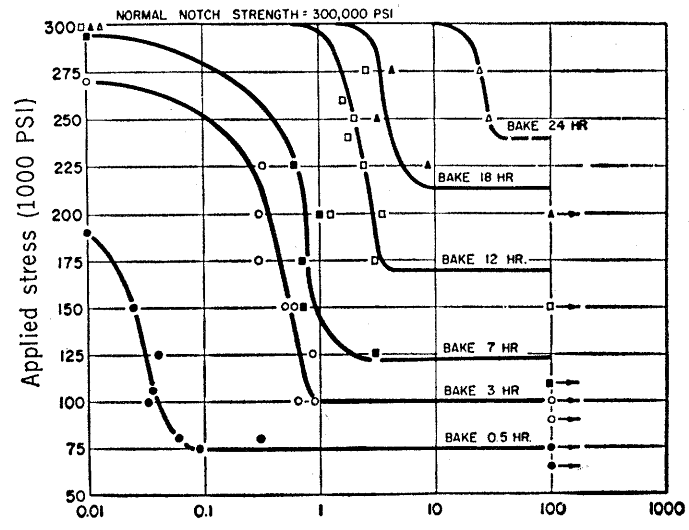


Fig. 4 (top left). Effect of charging time (hydrogen content) on ductility (*2*) of a high-strength steel heat-treated to various strength levels [1000 pounds per square inch (psi) = 70.3 kilograms per square centimeter]. [From Frohmberg *et al.* (*3*)]

Fig. 5 (top right). Fracture strain ϵ_f (*2*) of a mild steel without hydrogen, and containing hydrogen as a function of test temperature, for four different strain rates ϵ. [From Brown and Baldwin (*4*)]

Fig. 6 (left). Delayed failure of notched high-strength steel bars with different hydrogen contents corresponding to various baking times at 150°C [1000 pounds per square inch (psi) = 70.3 kilograms per square centimeter]. [From Troiano *et al.* (*5*)] fith argument, that during charging hydrogen creates these cracks by recombining to form gaseous molecular hydrogen at metal-inclusion interfaces, the resulting high pressure causing interface rupture and local formation of small cracks. The rapid growth of the cracks causes the pressure within them to drop, preventing further crack growth. In time the pressure once more increases from the continual diffusion and recombination of lattice hydrogen at the crack surface. The cracks can now be further extended, under the combined action of the stresses arising from increased pressure and the applied stress. As the cracks increase in size the remaining net section of metal supporting the load decreases until it can no longer withstand the increasing stress. At this stage fracture occurs rapidly, essentially independently of the hydrogen content of the metal, because of strain-rate effects. The total ductility exhibited by hydrogen-embrittled metal is, therefore, in part dependent on the ductility of the hydrogen-free metal. If the latter ductility is inherently low, very little additional deformation will occur at the onset of rapid failure. On the other hand, less-brittle metals like iron or mild steel have moderate ductility even when they are hydrogen-embrittled, because of the additional deformation after final failure begins. Tetleman's model is a more sophisticated version of earlier "pressure" models by Zapffe (*12*) and DeKazinczy (*13*).

Troiano (*6*) has proposed that hydrogen in solution diffuses to those local regions that are highly stressed elastically, particularly when the state of stress is such that there are tensile components in more than one direction. Such a state of stress would exist in the metal directly in front of a notch or crack. Incremental crack extensions at the relatively low stress observed to cause delayed failure would then occur only after sufficient hydrogen had accumulated near the crack tip to cause failure according to one of the aforementioned models. After an incremental extension, further growth is delayed until sufficient hydrogen has accumulated at the newly extended crack tip for the process to recur.

The proponents of each theory have substantiating experimental evidence, but no one hypothesis as yet proposed explains the mass of experimental data gathered to date, much of which is apparently contradictory. The reason for this is that two distinct areas of investigation are involved: (i) the effect of environment, structure, stress, testing conditions, and other factors on the solubility, diffusivity, and distribution of hydrogen in the metal, and (ii) the effect of these same environmental variables on the fundamental deformation behavior of the metal. Most important is the interaction between the deformation mechanism and the hydrogen which leads to embrittlement, but, because of limited knowledge of areas (i) and (ii), an effective description of their interaction is difficult.

Summary

Hydrogen interacts with many metals to reduce their ductility (*2*) and frequently their strength also. It enters metals in the atomic form, diffusing very rapidly even at normal temperatures. During melting and fabrication, as well as during use, there are various ways in which metals come in contact with hydrogen and absorb it. The absorbed hydrogen may react irreversibly with oxides or carbides in some metals to produce a permanently degraded structure. It may also recombine at internal surfaces of defects of various types to form gaseous molecular hydrogen under pressures sufficiently high to form metal blisters when the recombination occurs near the outer surface. In other metals, brittle hydrides that lower the mechanical properties of the metal are formed. Another type of embrittlement is reversible, depending on the presence of hydrogen in the metal lattice during deformation for its occurrence. Under some conditions the failure may be delayed for long periods. A number of different mechanisms have been postulated to explain reversible embrittlement. According to some theories hydrogen interferes with the processes of plastic deformation in metals, while according to others it enhances the tendency for cracking.

References and Notes

1. G. A. Nelson and R. T. Effinger, *Welding J. Res. Suppl.* **34**, 12-S (1955).
2. Quantitative measures of embrittlement and ductility vary. The most useful quantitative measures of ductility are the true fracture strain, ϵ_f, and the percentage reduction in area at fracture, R.A. For example, in a tension test of a bar, if the initial cross-sectional area is A_0 and the area at fracture is A_f then R.A. $= 100\ [1 - (A_f/A_0)]$ and $\epsilon_f = \ln_e(A_0/A_f)$. Embrittlement denotes reduction in R.A. or ϵ_f from a standard value for unembrittled metal, measured in the same units as ductility or measured as a percentage decrease. It is much less frequently referred to in quantitative terms than ductility is.
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12. C. A. Zapffe, *J. Iron Steel Inst. London* **154,** 123 (1946).
13. F. DeKazinczy, *ibid.* **177**, 585 (1954).
14. The broad treatment of the hydrogen embrittlement problem given here is a simplification, for the benefit of the general reader. Personal bias has no doubt been introduced, more by omission than commission, I hope, reflecting my own background and experience. I have deliberately kept the list of references small, but refer readers interested in a more detailed critical discussion of the various aspects of the subject to the following bibliography.

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