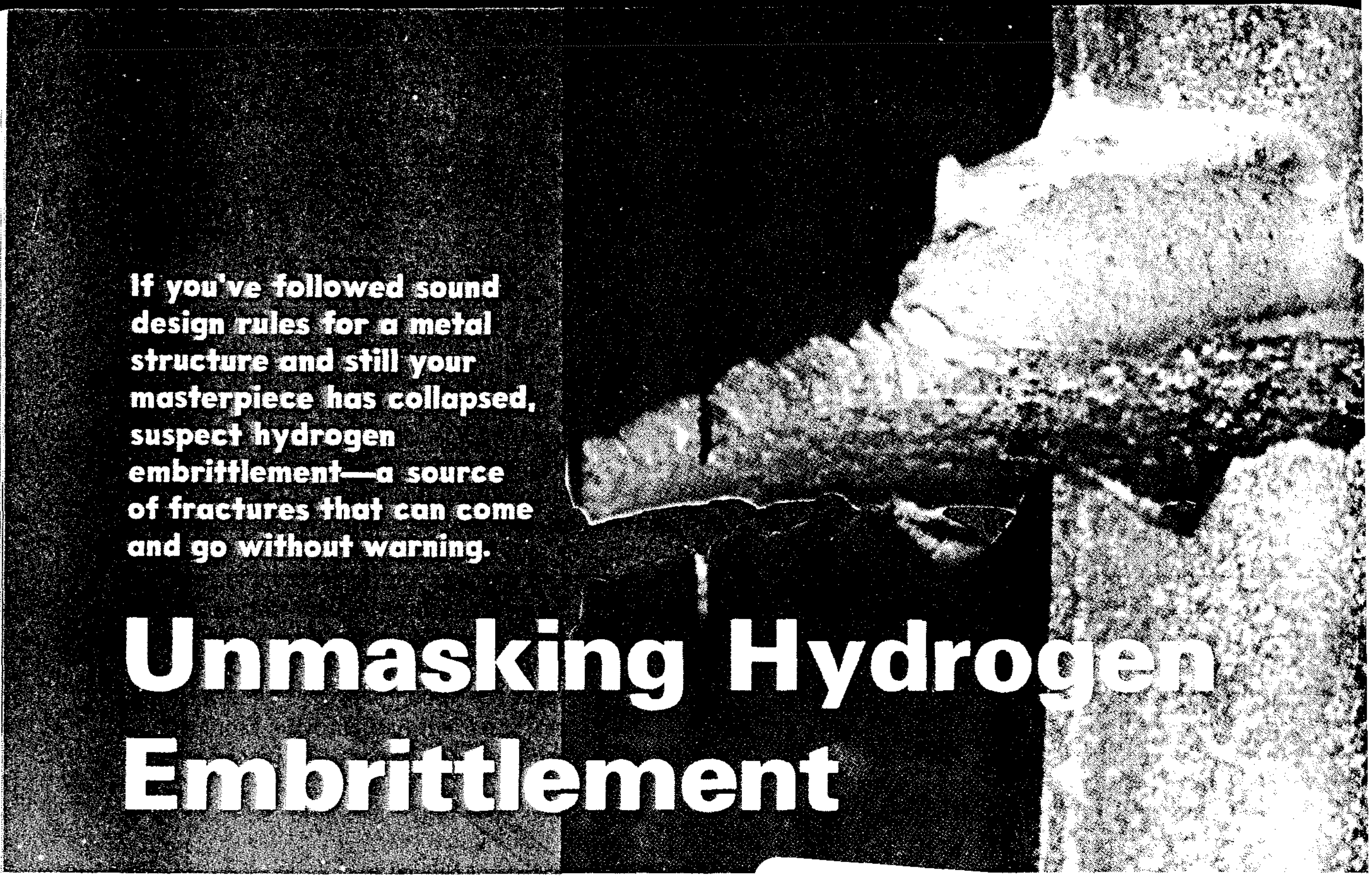

If you've followed sound design rules for a metal structure and still your masterpiece has collapsed, suspect hydrogen embrittlement—a source of fractures that can come and go without warning.

Unmasking Hydrogen Embrittlement

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HIGH-STRENGTH METALS such as titanium, zirconium, various steels, and 7075 aluminum, have been widely used where high strength-to-weight ratios are required, particularly in aerospace structures. Unfortunately, many of these materials can crack unexpectedly when infiltrated by hydrogen. The cause of these failures is often a mystery because the crack-inducing hydrogen can dissipate into the atmosphere before it is identified.

What Hydrogen Does

Hydrogen in these metals can cause one or a combination of the following maladies: decarburization of steel accompanied by methane generation that can cause internal fissuring and blistering; stress-corrosion cracking (even in the absence of external stress); formation of external hydride sheaths and internal hydride platelets in titanium and similar metals; and loss of ductility, decrease in yield stress, and the catastrophic static delayed failure.

All these phenomena are called hydrogen embrittlement (HE) although this term is frequently restricted to the loss of ductility and delayed failure (DF).

Decarburization occurs most often in low-alloy steels that are exposed to high temperatures and hydrogen, situations frequently found in chemical and nuclear applications. Decarburization causes structural deterioration and internal gas pressure that can lead to fissuring and blistering.[1]

This condition is alleviated by adding small amounts of titanium and vanadium to the steel which chemically combines with the carbon. Chromium and molybdenum also are effective alloying elements in tying up carbon to prevent embrittlement. Many stainless steels resist decarburizing; some of these are 304, 321, 347, 405, and 410.

Blistering has also occurred in pressure vessels fabricated from carbon steel and in chromium-steel liners. This occurs when atomic hydrogen collects at discontinuities such as laminations and combines to form molecular hydrogen—and blisters. (Hydrogen-gas pressures of several thousand psi have been measured in these vessels.) Rapid hydrogen introduction by severe cathodic charging (i.e. when a part is a cathode in an electrolytic bath) has resulted in gaseous hydrogen that caused vanadium wire to explode.

Stress-corrosion cracking (SCC) occurs in a material exposed to a corrosive environment while under stress. External or residual stresses may not be necessary for this process because the corrosion itself may produce local stresses. Also, the corrosion process may generate hydrogen in the region of induced stresses.[2]

SCC is a severe problem in the chemical industry, and metals that are susceptible include Type 301, 302, 304, 347 stainless, 280 maraging steel, 7075 aluminum, Ti-8Al-1Mo-1V titanium alloy, 10-19% Ni-Fe iron alloy, and 15% Cu-Fe. On the other

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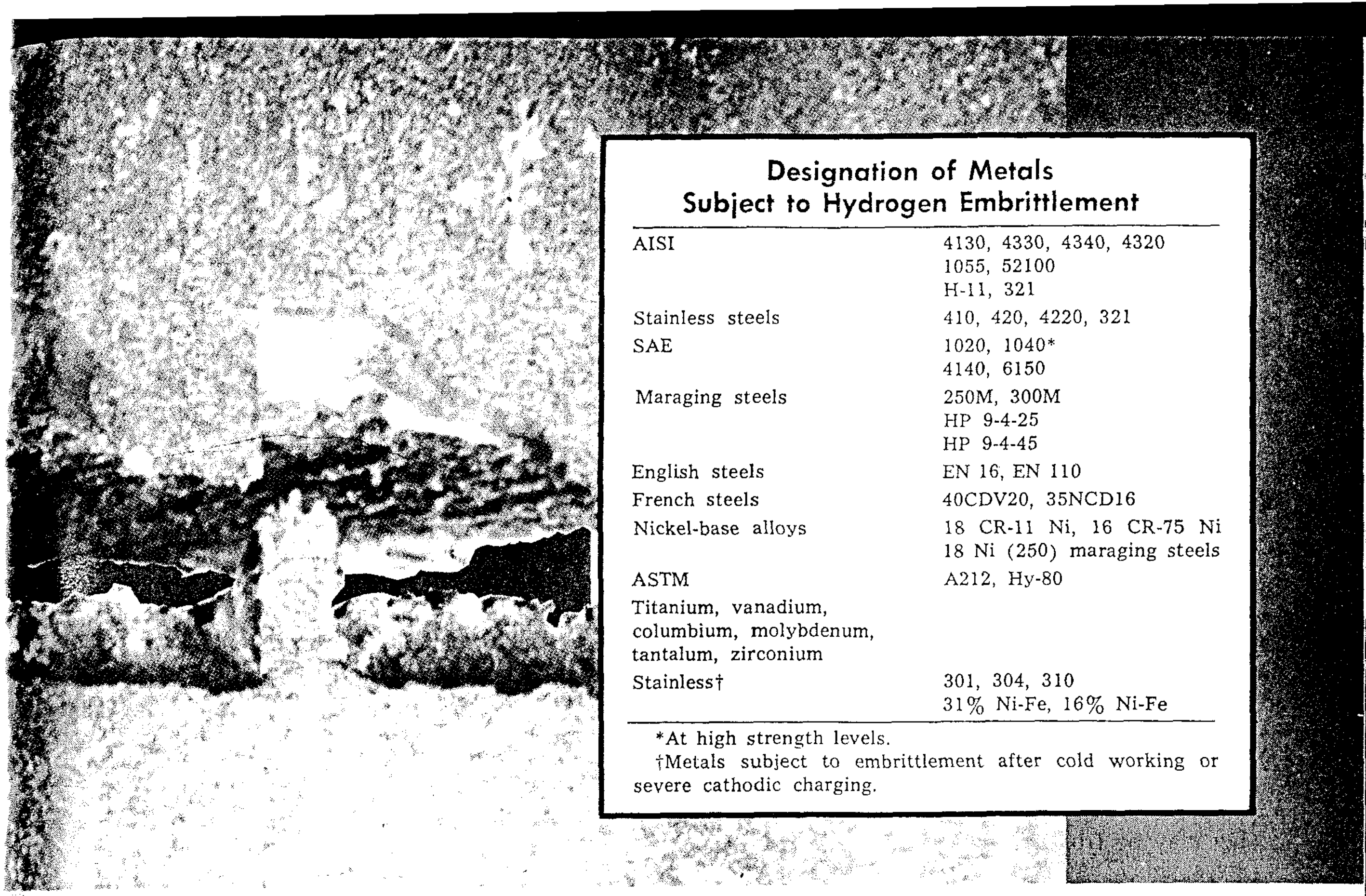
[1] References are tabulated at end of article.



Designation of Metals Subject to Hydrogen Embrittlement

AISI	4130, 4330, 4340, 4320 1055, 52100 H-11, 321
Stainless steels	410, 420, 4220, 321
SAE	1020, 1040* 4140, 6150
Maraging steels	250M, 300M HP 9-4-25 HP 9-4-45
English steels	EN 16, EN 110
French steels	40CDV20, 35NCD16
Nickel-base alloys	18 CR-11 Ni, 16 CR-75 Ni 18 Ni (250) maraging steels
ASTM	A212, Hy-80
Titanium, vanadium, columbium, molybdenum, tantalum, zirconium	
Stainless†	301, 304, 310 31% Ni-Fe, 16% Ni-Fe

*At high strength levels.
†Metals subject to embrittlement after cold working or severe cathodic charging.

hand, Type 316 steel, Inconel 600, and Ti-6Al-4V resist SCC. Vacuum remelting of 410 stainless steel markedly increases this material's resistance to SCC. Also, surface polishing of materials under anodic protection eliminates pits where corrosion might start. Cold rolling is also beneficial to low-carbon Ni-Fe alloys, the resistance being directional (resistance is greatest in direction of rolling), and beneficial effects decreasing with increasing carbon content.

Hydrides can form in titanium, zirconium, niobium, hafnium, and zircoloy — materials which are frequently used in high-temperature applications. Hydrides are low strength, brittle compounds that cause internal stresses due to the volume increases during their formation. The parent materials are frequently notch sensitive so that if a crack is initiated when the hydride is formed, it may easily propagate through the metal. This weakness may be amplified by the orientation of the hydrides with respect to the direction of stress; hydrides that form under residual stresses orient themselves perpendicular to the principal tensile stresses and parallel to compressive stresses. In this alignment, the hydride acts as as a crack in crack-sensitive material.

This condition lead to failure of welded joints in titanium pressure vessels in a spacecraft where the hydrogen was introduced into the material by welding. The welds failed when the vessel was pressurized.

Plastic deformation prior to hydride precipitation causes hydrides to align parallel to the direction of deformation; thus, some combination of plastic strain (prior to loading) and elastic residual

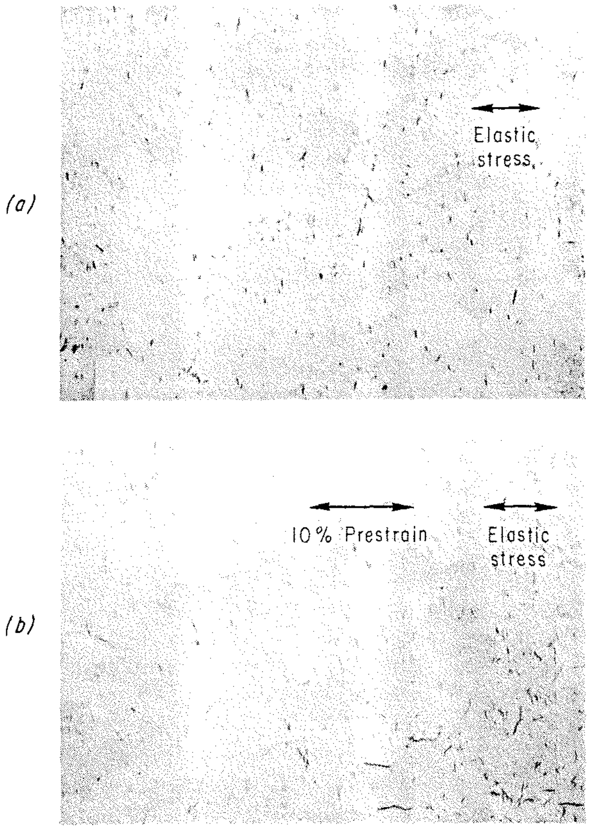


Fig. 1—Titanium alloy at 300x, showing orientation of titanium hydrides as black streaks. In photomicrograph *a*, alloy was not prestrained before loading; about 85% of the hydrides are oriented perpendicular to the direction of elastic stress. In photomicrograph *b*, alloy was subject to 10% plastic strain prior to service loading, thus disorienting the hydrides.

stress can cancel these directional effects. Combinations of prestrain and residual stresses on titanium cancel the directional properties successfully, Fig. 1.

An anomaly of hydrides is that a sheath created on the surface of some titanium alloys increases their ductility, perhaps by "filling in" surface scratches or flaws. In addition, some hydrides act as a hydrogen barrier, thus protecting the parent material from further hydrogen instrusion.

Static delayed failure (DF) of high-strength metals is the most serious result of hydrogen embrittlement. Here's what happens: A material with a given ultimate strength, yield stress, and ductility is stressed (either externally or residually) to some stress loading less than the yield stress and therefore thought to allow some margin of safety. However, if hydrogen is present in the material and the stress is greater than some minimum value known as the lower critical stress, then after some time delay, a brittle fracture will occur. The time delay may be from minutes to days, and the critical stress may be 20% of the yield strength. Very small amounts of hydrogen (as low as 5 ppm) will cause this behavior; then the hydrogen may vanish between failure and analysis of the part.

This behavior is particularly critical for the high-strength body-centered-cubic steels, but is not limited to them. A peculiar aspect of DF is that as you increase the yield strength of a material, the susceptibility to DF generally increases and the ratio of critical-to-yield strength decreases! This is shown in Fig. 2. The delayed failure curves are similar to the S-N curves of dynamic fatigue; thus the DF phenomena is sometimes referred to as static fatigue and the critical stress called the static endurance limit.

Hydrogen embrittlement must be prevented if the full yield strength of a material is to be used. The most effective way of insuring this is to prevent hydrogen from entering the material. An interesting aspect of this type HE phenomena is that if the hydrogen is removed from the material before the part is stressed, then no permanent damage will occur.[3]

How Hydrogen Gets In

What are the mechanisms by which hydrogen enters a material, and how can this entry be avoided? A possible source is the initial manufacture of a raw material, but the subsequent finishing processes, fabrication, and environmental conditions are the prime sources as the following examples illustrate:

Electroplating high-strength steels to protect them against corrosion is a chief cause of HE. By making the part cathodic in a plating solution containing water and an acid, hydrogen forms on the part surface, and frequently enters and embrittles the materials.

Hydrogen gas and hydrocarbons under pressure have caused failures in high-pressure storage tanks for space vehicles and less esoteric applications. In another example, ball bearings failed after picking up hydrogen from a hydrocarbon lubricant. Delayed failure was suspected in the failure of AISI 4340 oil driling rods where the hydrogen pickup may have been from the crude oil in the shaft.

Water and water vapor can introduce hydrogen into parts. A vessel used as a pressure bomb for a geologic experiment probably failed by HE after being forced over a liner immediately after machining in a water coolant. Failures of nuclear fuel elements, cladded by zirconium, have been traced to HE induced by pressurized cooling water.

Acid pickling to remove mill scale or chemical cleaning of materials can cause DF in steels. An English bolt and screw manufacturer found that DF occurred in parts manufactured from EN16 and EN110 steels that were blued by tempering in a steam environment. Also, coolants used in machining, grinding and abrading may introduce hydrogen.

Any circumstances in which hydrogen in almost any form is either present or produced on a metal surface may cause embrittlement. For instance, recording ink spread into cracks in 300M steels as a staining agent to obtain fracture toughness data has caused embrittlement.

Susceptible Materials

Delayed failure occurs primarily in body-centered-cubic materials such as the high-strength martensitic steels. In these steels, DF becomes more severe as the strength level is increased. In Fig. 2, DF is almost nonexistent at the lower strength level, and the difference between the unembrittled failure stress and the critical stress increases with strength.

Complicating the situation are some normally face-centered-cubic materials that may be transformed by cold working, plastic deformation, and severe electrolytic charging into materials that are susceptible to DF. In particular, stainless steels such as Type 301, 304, 310, and some nickel alloys are transformed into susceptible materials by cold rolling. Even old standbys such as 1020 steel are susceptible to DF if processed to high strengths (typically, 120 ksi). However, DF does not occur in fully austenitic steels. A listing of metals which have been embrittled is given in the table.

Delayed-Failure Mode

All the aspects of how embrittlement occurs are not known, but several characteristics of the mechanism have been defined. All materials have defects that act as stress raisers. When a combination of hydrogen and stress becomes critical, a

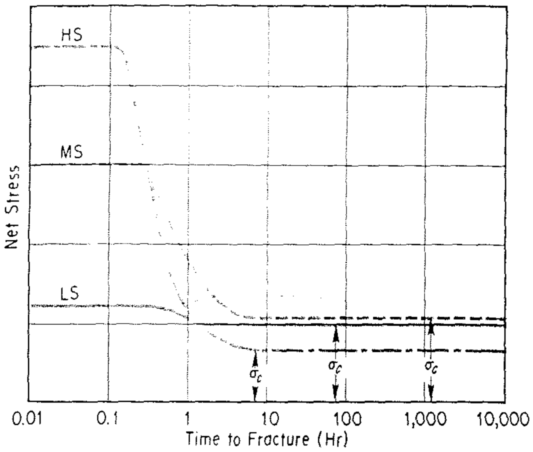


Fig. 2—Delayed failure for a steel heat treated to low (LS), medium (MS), and high-strength (HS) levels. Critical stress is σ_c.

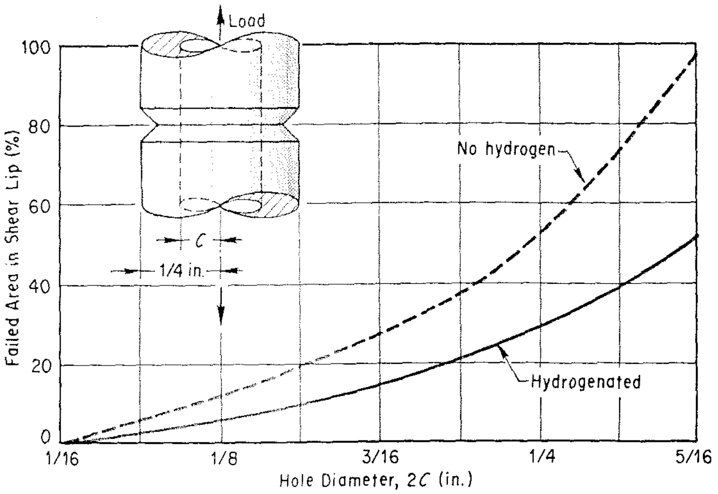


Fig. 3—Comparison of shear lip in fractures of embrittled and nonembrittled samples.

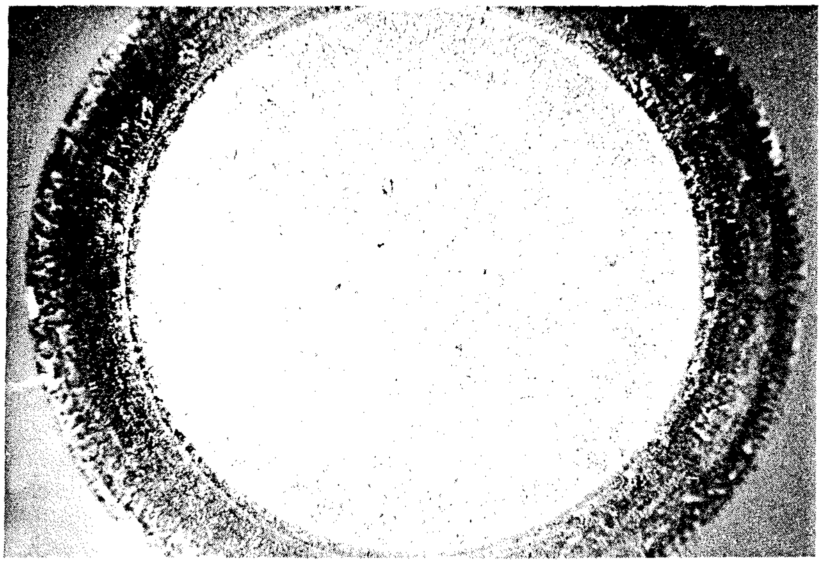


Fig. 4—Fractured titanium bar surface, showing area of slow crack growth (dark area) resulting from embrittlement, and area of sudden fracture.

crack starts at this point, and propagates away from the point of high hydrogen concentration and is subsequently arrested in a region of low concentration. The hydrogen then moves through the material along the stress gradients to the crack tip — the new stress-concentration point. When enough hydrogen collects here, the crack extends again. This process is repeated until the remaining cross section is reduced to the point where the part fails.

The diffusion of hydrogen from the old crack tip to the new tip requires a period of time from seconds to minutes (depending on the hydrogen available), and hence DF is sometimes called "slow strain-rate embrittlement." Embrittlement is most effective when strain rates are very low (i.e., allowing time for the hydrogen to accumulate at the crack tip) and at elevated temperatures (where diffusion rates are high)—opposite the more common embrittling effects of high strain rates and low temperatures. In fact, HE apparently disappears at very low temperatures.

Because a stress gradient must be maintained long enough for hydrogen to reach the crack tip, HE is not usually a factor in dynamic fatigue applications at zero mean stress. However, HE does shorten fatigue life if the mean stress is tensile, even though the mean stress is less than the critical stress. While DF is the most spectacular result of HE, other effects such as reduction of ductility and lowering of failure stress also occur.

Tracking Embrittlement

Determining if a failure is due to DF is difficult because the amount of hydrogen required for failure is small. Methods of determining these small amounts of hydrogen (typically, 5 ppm) are not always available, and furthermore, the hydrogen may escape from the material during the failure-examination interval.

Tests such as hot extraction and vacuum extraction of hydrogen are accurate to 0.1 ppm. Nuclear microprobe techniques can also be used. Tensile tests of parts suspected of HE indicate lowered ductility and notched tensile strengths. Sharply notched specimens increase the sensitivity of the tests. Testing in the inelastic region reduces strain hardening. Low-cycle fatigue testing (i.e., alternating stress in the inelastic range) may be a sensitive measure of HE; these tests show that the endurance limit of high-strength steels are reduced approximately 40% by presence of hydrogen.

Appearance of a fractured surface may reveal embrittlement. Less shear lip occurs on an embrittled surface than in nonhydrogenated materials, Fig. 3.

In some cases, the area of the failed surface in which slow crack growth occurs is somewhat darker than the surface where the final, rapid fracture occurs, Fig. 4. Unfortunately, such dark areas are not always present, thus limiting this factor as a diagnostic tool.

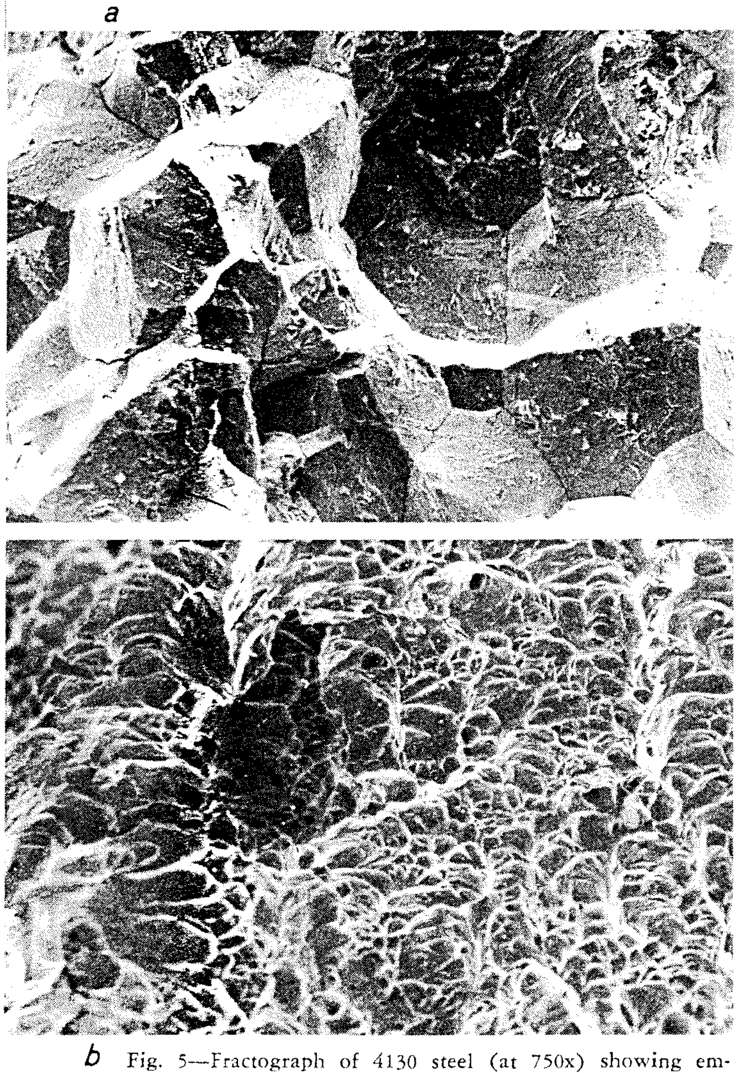


Fig. 5—Fractograph of 4130 steel (at 750x) showing embrittled material, *a,* and hydrogen-free material, *b.*

Fractographs, obtained with the scanning electron microscope, may also be useful. Fractographs of a slow-crack-growth surface, Fig. 5*a*, and one of the same material that was not embrittled by hydrogen, Fig. 5*b*, show marked differences in the fracture surfaces.

Prevention

The only effective way to avoid embrittlement is to prevent hydrogen from entering the material, to remove it prior to stressing, or to immobilize the hydrogen that is present.

One method of removing hydrogen is to age the metal at elevated temperatures. Frequently, ductility can be regained after baking at about 300 F, which is low enough that most materials are not softened, but high enough to allow reasonable recovery times. However, recovery of ductility is no guarantee that DF will not occur.

Plastic prestrain seemingly will raise the critical stress by providing lattice imperfections where hydrogen gas could be stored, thus preventing some hydrogen from reaching the crack tips. Shot-peening helps prevent DF in some materials.

Cadmium plating is a relatively good hydrogen barrier, but the electroplating process used to plate cadmium exposes the parts to hydrogen. Several new methods of plating are now available which can be used to plate susceptible materials. These methods include impact or peen plating which can be used to plate parts with zinc, cadmium, tin, lead, or brass powders; and nonaqueous baths where inorganic salts in an inorganic solution coat the metal surfaces. (Nickel and copper are applied by the second method.) Oxide coatings and hydride coatings may also act as hydrogen barriers.

Welding should be done on clean, bare metal with rods held in hot storage or rebaked if exposed to moisture. Thin beads should be deposited with a delay of up to one hour between passes; interpass temperature should be maintained to allow hydrogen to escape.

Blueing by tempering in carbon dioxide rather than steam eliminates the possibility of embrittlement from this process; or, when steam tempering must be used, high tempering temperatures reduce the degree of embrittlement.

Surface milling immediately after exposure to hydrogen removes most hydrogen because it does not have time to diffuse into the interior of the part. Parts that are to be anodically protected should be polished to remove points where corrosion—and hydrogen—might collect.

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