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THE EFFECTS OF HIGH-PRESSURE, HIGH-TEMPERATURE HYDROGEN ON STEEL

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Roger J. Runck

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DIRECTOR

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THE EFFECTS OF HIGH-PRESSURE, HIGH-TEMPERATURE HYDROGEN ON STEEL

by

E. E. Fletcher and A. R. Elsea

to

OFFICE OF THE DIRECTOR OF DEFENSE
RESEARCH AND ENGINEERING

DEFENSE METALS INFORMATION CENTER
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SUMMARY

This report deals with the deleterious effects of hydrogen gas on steel at elevated temperatures and/or pressures. Hydrogen attack on steels is manifest as decarburization, intergranular fissuring, or blistering. These conditions result in lowered tensile strength, ductility, and impact strength. The reaction of hydrogen with iron carbide to form methane is probably the most important chemical reaction involved in the attack on steel by hydrogen.

Steel can be heated to moderately elevated temperatures in gaseous molecular hydrogen at 1-atm pressure without being permanently damaged. However, decarburization occurs at higher temperatures. Moist hydrogen is more effective in decarburizing steel than is dry hydrogen. Steels containing strong carbide-forming elements resist this effect.

At ordinary temperatures, hydrogen gas can be handled safely in carbon-steel equipment at pressures up to several thousand psi, but, as the pressure approaches about 30,000 psi, severe embrittlement can occur. Once penetrated by hydrogen, the steel may be penetrated subsequently at far lower pressures. Austenitic stainless steel and beryllium copper are especially resistant to hydrogen under these conditions.

Under combined high temperatures and pressures, hydrogen or gas mixtures containing appreciable hydrogen can be especially destructive to many steels. Decarburization and the formation of many microscopic fissures can seriously weaken the steel. With the partial pressures of hydrogen that obtain in certain industrial processes, coarse-grained carbon steels are attacked slightly during long-time exposure at temperatures as low as 390 F, and the attack usually is severe at temperatures of 570 F and above. However, certain Cr-Mo steels are resistant to hydrogen attack at much higher temperatures, and austenitic stainless steels are especially resistant.

Factors that determine the degree of attack are temperature, hydrogen partial pressure, stress, exposure time, composition of the steel, and structure of the steel. For a given exposure time, hydrogen attack of steel starts at a limiting temperature and pressure. Longer exposure times permit attack to start at lower temperatures and pressures. Also, the higher the temperature, the lower is the limiting pressure, and the higher the pressure, the lower is the limiting temperature. The rate of hydrogen attack increases with increasing temperature and pressure, the rate being more sensitive to temperature changes than to pressure changes. Either prior cold work or creep during exposure accelerates the attack. The kinetics of the irreversible hydrogen attack of iron and steel appear to be different in two different temperature ranges and, also, for materials with and without carbon.

Attack of steel at elevated temperatures and pressures is limited or prevented by the following measures: (1) use of steel alloyed with strong carbide-forming elements, (2) use of liners of resistant alloy steels, and (3) substitution of resistant nonferrous alloys.

— INTRODUCTION

Certain gases, particularly hydrogen, oxygen, nitrogen, carbon monoxide, ammonia, hydrogen sulfide, and chlorine, have deleterious effects on metals at elevated temperatures and pressures. Therefore, a knowledge of these effects is important if equipment is to be designed to handle such gases safely under these conditions. This report is concerned only with the action of hydrogen, or mixtures of hydrogen with other gases, on steel at various temperatures and pressures.

Under certain conditions, hydrogen is able to permeate solid steel. Dissociated, or atomic, hydrogen can enter steel, diffuse through it, and leave again. Sometimes it leaves evidence in the form of either temporary or permanent damage to show that it has been present in the steel. At ambient temperatures, nascent (atomic) hydrogen released at the surface of steel by certain corrosive agents, such as acids or water, or by electrochemical action can permeate and damage steel. The damage consists of loss of ductility, loss of load-carrying ability (particularly for high-strength steels), and sometimes cracking and blistering. Gaseous molecular hydrogen does not readily permeate steel at ambient temperatures, not even at pressures up to several thousand pounds per square inch.

At high temperatures and pressures, the molecular hydrogen is partially dissociated into the atomic form, the degree of dissociation increasing as the temperature increases. This atomic hydrogen from thermal dissociation also can enter the steel and can cause either temporary or permanent damage. The embrittlement during the initial stages of the permanent damage, which is brought about by the entry of hydrogen in this way, usually is not as drastic as the low-strain-rate embrittlement caused by hydrogen introduced at temperatures below about 450 F.

The damage to steel usually is only temporary if the hydrogen is driven out of the steel by a suitable thermal treatment before decarburization, blistering, or cracking begins. For high-strength heat-treated parts or electroplated parts, such thermal treatments may not be feasible or completely effective. In steels for service at elevated temperatures, such treatments usually are effective but may not be feasible, for example, in the case of large equipment in the field. However, once decarburization, intergranular cracking, or blistering has occurred, the damage is permanent; the steel loses tensile strength by decarburization and cracking, and the part becomes permanently embrittled as the result of crack formation.

Examples of thermal treatments that have been used to drive off hydrogen are 2 hours at 1200 F and 24 hours or so at 225 to 375 F. Hydrogen will effuse from steel at room temperature, given a long enough time. For example, it was observed that 60 days at room temperature was required to reduce the hydrogen to the "equilibrium" level in 1-inch-square cast coupons of carbon steel. The diffusion rate varies inversely as the square of the thickness, so the size of the part is an important factor in selecting a treatment to eliminate hydrogen.

It can be said that there are two important aspects to the problem of steel exposed to hydrogen at high temperatures and pressures: (1) a purely physical action involving penetration of hydrogen into the crystal lattice with consequent disruptive effects, and (2) a chemical reaction between hydrogen and various elements present in steel, primarily carbon. The former effect can occur at room temperature in the case of nascent (atomic) hydrogen liberated by chemical attack or corrosion, or it can occur at high temperatures, high pressures, or intermediate temperatures combined with high pressures in the case of molecular hydrogen, which undergoes some dissociation under these conditions. Two aspects of the physical action of hydrogen on steel, namely hydrogen embrittlement and delayed, brittle failure, have been the subject of separate reports (DMIC Memorandum No. 180 and DMIC Report No. 196) by the authors of the present report.

Chemical action, such as decarburization, does not take place at the lower temperatures. Chemical activity occurs at elevated temperatures and is accelerated by high pressures. The present report deals primarily with the chemical attack of steel by hydrogen.

Those general characteristics of hydrogen occlusion which are believed to relate to all occlusive metals, including endothermic occluders (such as iron) and exothermic occluders as well, have been listed by D. P. Smith(1) as follows:

(1) Metal, in its ordinary state, is inert toward gaseous hydrogen, at ordinary temperature and pressure.

(2) If gradually heated in hydrogen, the metal begins to occlude at a (rather indefinite) "opening temperature".

(3) Occlusion is, in its earlier stages, self-accelerating ("initial opening").

(4) Metal, in its ordinary state, is penetrated by hydrogen at extreme pressures and, when once thus opened, is thereafter permeable at much lower pressure.

(5) Metal in its ordinary state, although impermeable to gas at atmospheric pressure, readily occludes hydrogen liberated upon it electrolytically or by chemical displacement (that is, in the atomic form).

(6) Repeated absorption and evolution of hydrogen cause either much diminished or much increased permeability, depending, apparently, upon the rapidity with which the gas is expelled.

(7) Metal which has been subjected to high heating is very inert to the gas; and, particularly, pure metal, after such heating in a vacuum, may be impervious even to cathodic hydrogen.

(8) Permeability is increased by plastic deformation, sometimes manyfold.

(9) Increase of permeability, however produced, is accompanied by increase of occlusive capacity.

The fourth of these characteristics had been directly shown only for iron at the time of Smith's writing. The rest are more broadly based. His list of special characteristics of exothermic occluders is not pertinent to the present discussion, because iron is an endothermic occluder. The differences between the two types of occlusion will be discussed in a separate report on the movement of hydrogen in iron and steel.

At room temperature, the solubilities of hydrogen in iron and the other endothermic occluders are very small. However, the solubilities increase with increasing temperature and sometimes become considerable at red heat and above. For example, see the curve for iron for a hydrogen pressure of 1 atm in Figure 1.

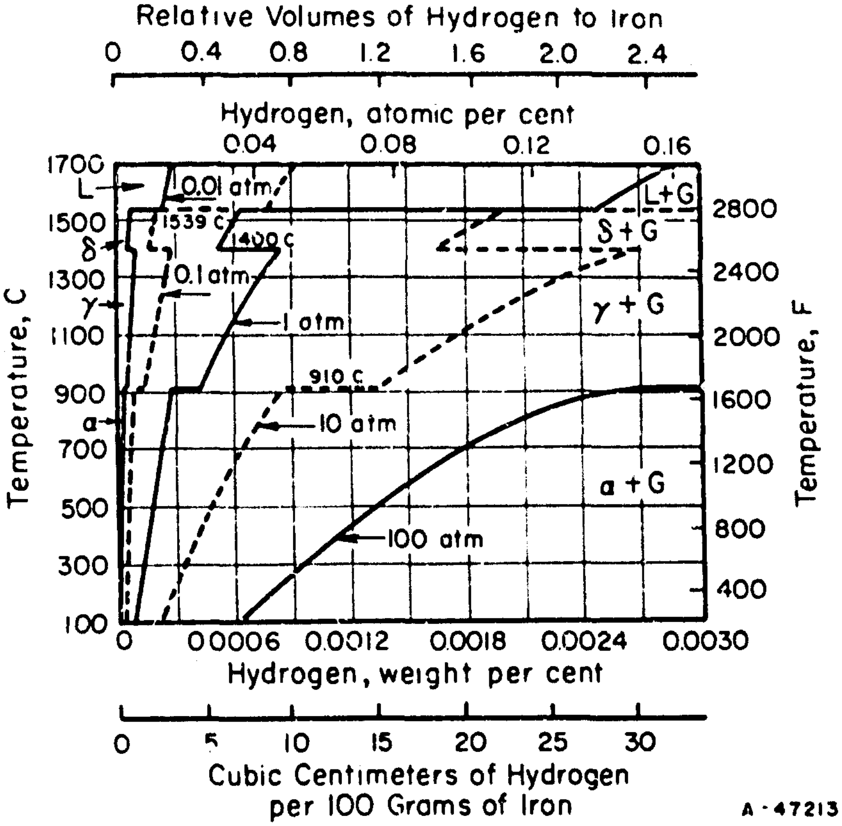


FIGURE 1. Fe-HIRON-HYDROGEN CONSTITUTIONAL DIAGRAM(2)

The solubility of hydrogen in solid steel (and liquid steel as well) obeys Sieverts' law, that is, it varies as the square root of the pressure of molecular hydrogen (H_2). The reason for this is that hydrogen dissolves in the atomic form, not the molecular form, and the H_2 must dissociate to 2H. The solubility relationship is given by

$$[H] = K \cdot (P_{H_2})^{1/2} .$$

Figure 1 shows the effect of hydrogen pressures up to 100 atm on the solubility of hydrogen in iron.

Thus, iron is inert to ordinary gaseous hydrogen at room temperature and 1-atm pressure. However, by heating to elevated temperatures where some dissociation of the hydrogen occurs, the solubility is increased considerably. Heating in high-pressure hydrogen increases the solubility still further. This is one method that has been used to introduce hydrogen into steel for studying hydrogen embrittlement and delayed, brittle failure. The solubility of hydrogen in solid steel decreases with decreasing temperature, and steel that has been saturated at a high temperature will retain hydrogen above the solubility limit if it has been cooled rapidly or if the section size is large. Under certain other conditions, hydrogen may be occluded in quantities far greater than its solubility. This is referred to by some as surcharging. This may occur when cold-worked steel is exposed to hydrogen, when annealed steel is exposed to cathodic or chemically liberated hydrogen (that is, atomic hydrogen), or when iron is electrodeposited under conditions of electrolysis that favor co-liberation of atomic hydrogen.

Highly purified iron that has been annealed for prolonged periods at high temperature is impermeable to either molecular or atomic hydrogen at room temperature(1, 3). However, cathodic hydrogen is readily absorbed, and in quantity, by such otherwise inert iron when cathodic poisons such as arsenic, H_2S, or phosphorus are added to the electrolyte. High-purity iron, rendered inert by annealing, at once recovers its ability to occlude hydrogen in quantity upon being moderately cold worked.

HYDROGEN AT HIGH TEMPERATURES AND NORMAL PRESSURE

Moore and Smith(3) soaked thin, cold-rolled strips of carbonyl iron in high-purity hydrogen at 1 atm and 25 C (77 F) for 55 days. The strips were found to have occluded 45 relative volumes of hydrogen, or 200 times as much hydrogen as could be accounted for by true lattice solubility. From this evidence, they concluded that a large amount of occlusion occurs in rifts or voids. However, the quantity of hydrogen retained on thermal charging is limited to the solubility in solid steel at the charging temperature, but the retention curve appears to fall below the solubility curve with increasing temperature(4, 5, 6).

At low pressures, gaseous molecular hydrogen can be heated to moderately elevated temperatures without causing damage to steel.

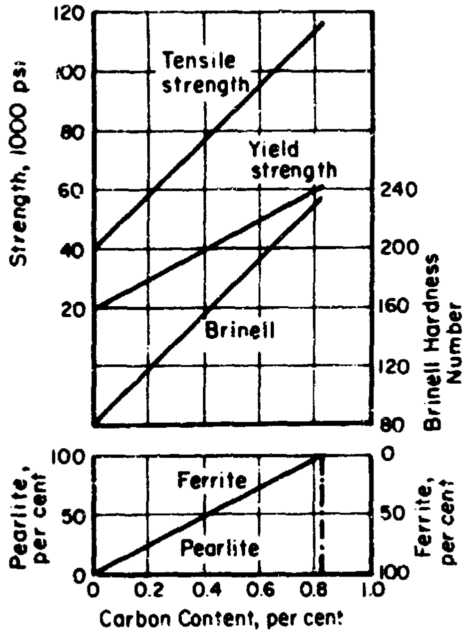
According to Johansson and von Seth,(7) Forquignon in 1881 was the first to discover that decarburization of steel took place in a hydrogen atmosphere (in nitrogen as well). Wüst and Geiger in 1905(8) were unable to duplicate Forquignon's results. However, Wüst and Sudhoff in 1910(9) suggested that small amount of oxygen or water vapor may have been present in the gases used by Forquignon which would account for the decarburization he obtained. As early as 1900, Heyn(10, 11, 12) observed embrittlement of iron by hydrogen that was retained in the iron after heating in hydrogen at a high temperature (above 730 C, or 1345 F) followed by quenching without exposure to air. He found 0.00019 per cent of hydrogen. This retention of hydrogen introduced at high temperatures was confirmed by the work of Luckemeyer-Hasse and Schenck(13). Even the presence of only small amounts of hydrogen in the atmosphere of an annealing furnace has been reported to cause embrittlement of steel(14, 15, 16, 17). Bardenheuer and Ploum(4) found that steel wire heated in hydrogen was embrittled, as demonstrated by bend and torsion tests at room temperature, but a similar treatment in a nitrogen atmosphere did not result in a similar loss of properties.

Studies of the controlled atmospheres used in industrial heat-treating and decarburizing operations have revealed the effect of hydrogen on impurities in steel. Such studies have established that the effectiveness of hydrogen in removing carbon from steel is influenced by the amount of moisture in the hydrogen.(18-22) Buzzard and Cleaves(23) suggested that failure to recognize that moisture is a factor in decarburization may account for the divergent conclusions of early investigators as to whether hydrogen does (Forquignon, 1881; Cely, 1883; Ledebur, seven papers between 1886 and 1891; and Stead, three papers between 1882 and 1884) or does not (Heyn, three papers 1900 to 1903, Wüst and Geiger, 1905; Emmons, 1914; and Wüst and Sudhoff, 1910) remove carbon from iron-carbon alloys. Subsequent investigations have established that hydrogen does decarburize iron-carbon alloys and have provided much information on the effect of water vapor on the reaction. Buzzard and Cleaves give 25 references to such investigations. Baukloh and co-workers(24,25,26) did considerable work on the decarburization of iron-carbon alloys by hydrogen. Among the more notable investigations of the decarburization of steel with hydrogen and water vapor are those listed in References 27,21,28,19,29,30,22, and 31.

Several early investigators studied the action of hydrogen at high temperatures and normal (1 atm) pressure on mild steel, for example Campbell(27), Whiteley(32), and Austin(28). The results of these various investigations showed that diffusion of hydrogen into steel removed carbon, oxygen, and sulfur. The effect was especially pronounced for carbon. Because carbon exerts such a strengthening effect on steel, its removal by hydrogen is the principal weakening effect involved in the phenomenon known as "hydrogen attack". The serious consequences of decarburization on the tensile strength, yield strength, and hardness of steel can be seen by examining Figure 2 which shows the relationship between the mechanical properties of slowly cooled carbon steels and the carbon content. This figure also shows how the strength is related to the relative proportions of ferrite and pearlite in the microstructure of such steels. Figure 3 shows how the hardness of plain-carbon steels quenched and subsequently tempered at high temperatures depends on the carbon content (the strength is directly related to the hardness). Figure 4 shows decarburization and changes in hardness in the wall of a catalyst container used to synthesize ammonia. Note how the hardness depended on the carbon content, the two curves being nearly parallel.

Some of these early investigators found that elements such as chromium form carbides that are more stable in the presence of hydrogen than is iron carbide (Fe_3C, also called cementite). They also learned that the removal of the carbon occurs by the formation of methane, CH_4, and that an equilibrium exists between the carbon present in the steel, the hydrogen, and the product of the reaction (CH_4). Austin(28) showed that there exists a limiting temperature range below which attack is very slow (see Figure 5). An increase of pressure would be expected to reduce this temperature limit, and such has been found to be the case.

Campbell(27) studied the decarburization of 12 steels with hydrogen. Both plain-carbon and alloy steels were included, and the carbon contents ranged from 0.094 to 1.67 per cent. The compositions of the steels are listed in Table 1. The steels were exposed to hydrogen at 1-atm pressure for from 4 to 12 days at a temperature of 950 to 1000 C (1740 to 1830 F); for one steel the temperature range was 950 to 1050 C (1740 to 1920 F). Table 2 shows some of the results obtained and indicates the extent of decarburization and desulfurization obtained. The 4Cr-5Mo steel (Steel L) was the most resistant to decarburization. However, 12 days exposure at 950 to 1050 C (1740 to 1920 F) served to reduce the carbon content of this steel from 1.67 to 0.22 per cent. This steel contained appreciable percentages of two elements which form carbides that are much more stable than is iron carbide. Campbell demonstrated that moist hydrogen was more efficient at decarburization than was dry hydrogen. When he added carbon dioxide to the hydrogen in amounts up to 50 per cent, decarburization was not accelerated at any temperature or any concentration studied.



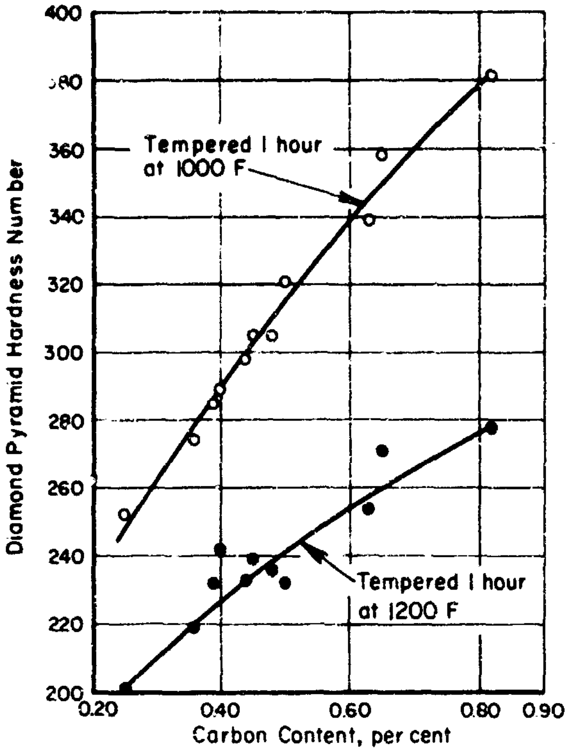
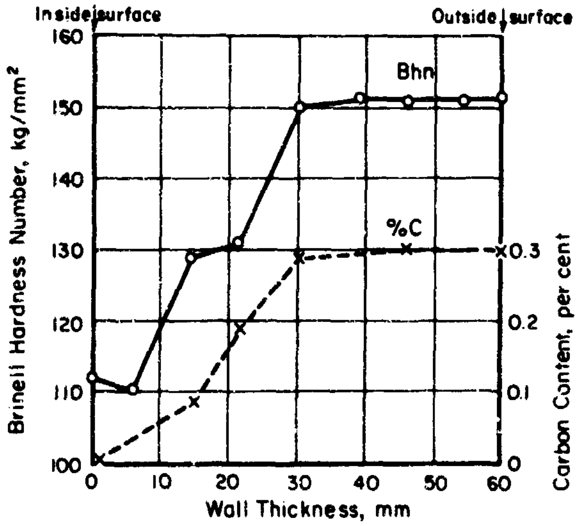


FIGURE 2. RELATION OF MECHANICAL PROPERTIES AND STRUCTURE TO CARBON CONTENT OF SLOWLY COOLED CARBON STEELS

After Rosenberg and Digges.(33)

FIGURE 3. DEPENDENCE OF HARDNESS OF QUENCHED-AND-TEMPERED PLAIN-CARBON STEELS ON THE CARBON CONTENT

After Grange and Baughman.(34)



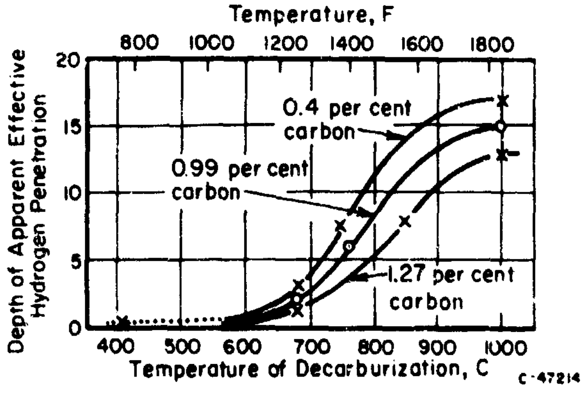


FIGURE 4. DECARBURIZATION AND CHANGES IN HARDNESS IN THE WALL OF A CATALYST CONTAINER, 60 MM THICK, FOR AMMONIA SYNTHESIS

After Naumann.(35)

FIGURE 5. EFFECT OF TEMPERATURE ON APPARENT DEPTH OF HYDROGEN DECARBURIZATION OF THREE CARBON STEELS, WITH A CONSTANT TIME FACTOR OF 12 HOURS(28)

The ordinates are divisions on the micrometer eyepiece for a fixed objective and magnification.

TABLE 1. ANALYSES OF 12 STEELS USED TO STUDY DECARBURIZATION WITH HYDROGEN(27)

Steel	Composition, per cent C	Mn	P	S	Si	Ni	Cr	W	Mo
A	1.184	0.016	0.005	0.018	--	--	--	--	--
B	0.094	0.122	0.03	0.025	3.649	--	--	--	--
C	1.02	0.275	0.697	0.046	0.314	--	--	--	--
D	1.150	11.57	0.055	0.023	0.25	--	--	--	--
E	0.354	0.486	0.012	0.026	0.162	1.50	0.57	--	--
F	0.422	0.677	0.038	0.030	0.231	2.80	--	--	--
G	0.365	0.660	0.027	0.034	0.226	3.43	--	--	--
H	0.362	0.405	0.013	0.026	0.162	4.48	--	--	--
I	0.182	0.493	0.010	0.030	0.267	5.00	--	--	--
J	1.05	0.38	0.007	0.011	0.45	--	1.40	--	--
K	0.683	0.32	0.018	0.016	0.12	--	0.24	5.04	--
L	1.67	0.33	0.013	0.042	0.90	--	3.98	--	5.07

TABLE 2. RESULTS OF EXPERIMENTS ON THE DECARBURIZATION AND DESULFURIZATION OF STEEL WITH HYDROGEN(27)

Steel	Temperature of Furnace, C	 F	Time of Decarburization, days	Carbon Content, per cent Before	 After	Sulfur Content, per cent Before	 After	Specific Resistance at 25 C (77 F), microhms Before	 After
A	950 - 1000	1740 - 1830	8	1.184	0.005	0.018	0.006	15.88	11.00
B	950 - 1000	1740 - 1830	4	0.094	0.076	0.025	0.017	54.10	53.60
C	950 - 1000	1740 - 1830	8	1.02	0.045	0.046	0.032	30.12	25.00
D	950 - 1000	1740 - 1830	12	1.150	0.133	0.023	0.026	53.85	51.93
E	950 - 1000	1740 - 1830	5	0.354	0.017	0.026	0.014	22.33	21.82
F	950 - 1000	1740 - 1830	4	0.422	0.036	0.030	0.020	26.76	25.40
G	950 - 1000	1740 - 1830	5	0.365	0.020	0.034	0.028	26.80	25.67
H	950 - 1000	1740 - 1830	4	0.326	0.027	0.026	0.018	25.43	24.19
I	950 - 1000	1740 - 1830	5	0.182	0.015	0.030	0.017	28.63	26.78
J	950 - 1000	1740 - 1830	5	1.05	0.035	0.011	0.003	24.20	26.57
K	950 - 1000	1740 - 1830	5	0.683	0.026	0.016	0.006	19.52	24.30
L	950 - 1050	1740 - 1920	12	1.67	0.220	0.042	0.008	40.03	54.73

Austin(28) studied the decarburization of three carbon steels with 0.40, 0.99, and 1.27 per cent carbon in hydrogen at 1-atm pressure and at various temperatures generally between 680 and 1000 C (1255 to 1830 F). Figure 5 shows the effect of temperature on the depth of hydrogen decarburization. The depth used was that at which any effect on the carbide constituent was discernible under the microscope. The ordinates on the figure are divisions on the micrometer eyepiece for a fixed objective and magnification. The effect of time on the depth of decarburization is shown in Figure 6.

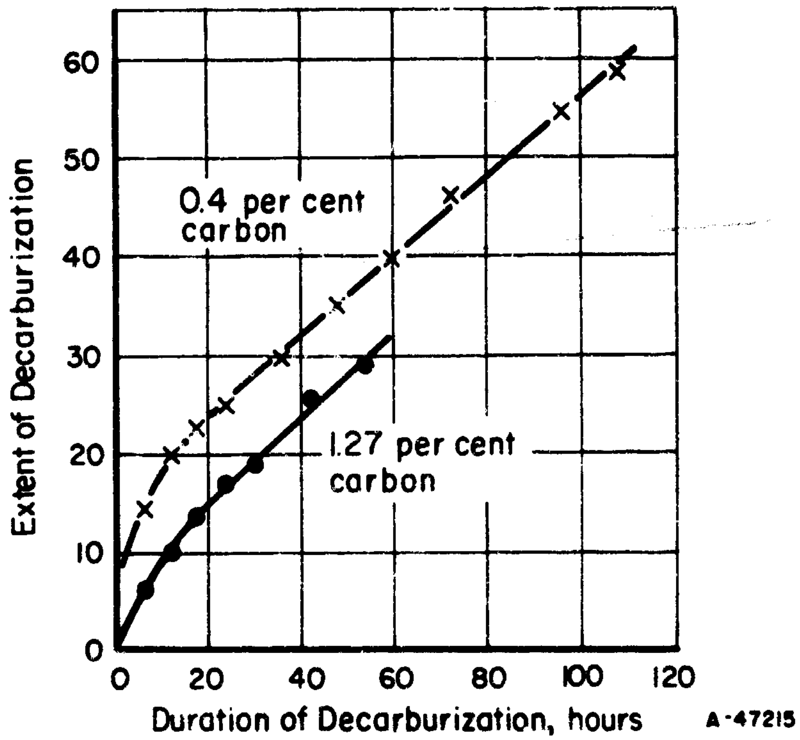


FIGURE 6. EFFECT OF TIME ON DEPTH OF DECARBURIZATION AT 680 C (1255 F)(28)

The ordinates are divisions on the micrometer eyepiece for a specific objective and magnification.

Campbell, Ross, and Fink in 1923(18) were among the first to show that the double carbides of iron and chromium were more resistant to the decarburizing action of high-temperature hydrogen than is cementite (Fe_3C).

Cioffi(36, 37) studied the effects of heating in hydrogen at high temperatures on the magnetic properties of iron, particularly the magnetic permeability. The treatment increased the magnetic permeability markedly. He found the greatest effect when the iron was heated near 1500 C (2730 F) for 30 minutes in hydrogen that had been saturated with water vapor at room temperature, and then was rapidly cooled to just below the A_3 point of pure iron and annealed at this temperature for some time. Cioffi attributed the improved magnetic permeability to the decarburization and general purification effected by the treatment in hydrogen, more than to the residual hydrogen content, which must have been quite small(37).

In their early studies of decarburization with high-temperature hydrogen, Campbell, Ross, and Fink(18) showed that not only is moist hydrogen more efficient than dry hydrogen in decarburizing at 950 C (1740 F), but their results indicated that the moisture is essential to complete decarburization at this temperature and 1 atm of hydrogen.

In annealing low-carbon deep-drawing auto-body sheet steel in wet hydrogen to eliminate completely the yield-point elongation typical of these steels, Low and Gensamer(22) found that the principal changes in composition were a marked lowering of the carbon and nitrogen contents while the oxygen content was either unaffected or increased slightly. They found that the optimum temperature for the treatment was 720 C (1330 F). The effectiveness of the hydrogen in removing carbon and nitrogen and in eliminating the yield point and strain aging (phenomena which depend on the presence of carbon and nitrogen) was markedly affected by the presence of water vapor in the hydrogen, as is shown in Table 3. Thus, the time of treatment was relatively short when the water content of the hydrogen atmosphere was made fairly high, say almost 30 per cent by volume.

TABLE 3. TIME REQUIRED FOR ELIMINATION OF YIELD POINT AND STRAIN AGING USING VARIOUS MIXTURES OF HYDROGEN AND WATER VAPOR(22)

Temperature 710 C (1310 F); material 0.0335-in. cold-reduced rimmed steel.

H_2O (Bal H_2), vol%	Time to Eliminate Strain Aging, hr	Time to Eliminate Yield Point, hr
Tank H_2(a)	20	140
4.7	2.5	3.0
7.5	2.0	2.5
21.0	1.5	2.0
29.1	1.5	1.5

(a) Less than 0.001 per cent H_2O.

Pennington(31) studied the decarburization of steel by wet hydrogen, with particular attention being given to the mechanism of the reaction. He studied the decarburization of a plain-carbon steel of eutectoid composition at temperatures from 1275 to 1700 F, generally at temperature intervals of 50 degrees. A mixture of hydrogen and water vapor containing approximately 20 per cent of water vapor by volume was used to effect decarburization. His paper contains a number of photomicrographs showing the progress of decarburization with time at the different temperatures and, also, the general nature of the phenomenon at the different temperature levels. Pennington discussed the chemical reactions pertaining to decarburization of steel; he favors the following reaction as being the one responsible for the decarburization in a mixture of gaseous hydrogen and water vapor:

$$C \text{ (in sol.)} + H_2O = CO + H_2 \ .$$

Thus, he regarded water vapor as a reactant, not a catalyst.

Pennington pointed out that two general mechanisms have been proposed by various investigators to explain decarburization of steel, as follows:

(1) The removal of carbon by the diffusion of gases, such as hydrogen, oxygen, water vapor, and carbon dioxide, into the interior of the steel where a reaction takes place with iron carbide at a subsurface to form iron and carbon monoxide or methane, and the subsequent diffusion of the resultant gases to the surface of the metal.

(2) The removal of carbon by its diffusion through gamma or alpha iron, in the form of dissolved iron carbide, to the surface, at which place gaseous compounds of carbon are formed, thus rendering the steel less rich in carbon.

Some investigators believe that both principles are at work simultaneously, diffusion of gases predominating at the lower temperatures, and diffusion of carbon predominating at the higher temperatures. Baukloh and co-workers(24,25,26) did considerable work on the decarburization of iron-carbon alloys by hydrogen. They explained the phenomenon on the basis of the permeability of hydrogen. Jominy(29), Austin(21), Webber(38), and others believed that the observed formation of definite bands of ferrite underneath the surface of the steel is evidence that the decarburizing gases diffuse into the steel and react at an interface from which the carbon monoxide diffuses to, and is liberated at, the surface. Baukloh and Knapp(39) maintained that the gas diffusion predominates up to 1560 F, at which temperature the diffusion of the dissolved carbon is faster than that of the gases and, therefore, ferrite banding does not occur when the decarburization is carried out above 1560 F. However, Pennington working with eutectoid carbon steel found banding up to about 1650 F, and, according to Pennington, Naito working with white cast iron also found banding up to about the same temperature. Rowland and Upthegrove(30) and Ledebur in 1898 reasoned that dissolved oxygen may diffuse into the steel to the reacting interface.

Both Yensen and Sims in discussing the paper of Rowland and Upthegrove expressed doubt that the decarburizing reaction takes place at some subsurface interface within the steel. Sims contended that the carbon diffuses through the ferrite as iron carbide, and that the chemical reaction takes place at the surface of the steel. However, he did not account for the formation of the observed ferrite bands. Averbukh and Chufarov(40) also contended that the carbon arrives at the surface from the interior of the steel by diffusion in solid solution. Pennington(31) cited a number of arguments to support his belief that the gas-diffusion theory is untenable. One argument was that copper-plated steels do not decarburize so long as the plate exists, in spite of the fact that gases, including hydrogen, diffuse in copper. He regards carbon as reaching the surface by diffusing in solid solution as either dissolved elementary carbon or iron carbide, regardless of whether the iron is in the austenitic or ferritic condition. The chemical reaction at the steel surface which results in carbon removal results in the carbon gradient that provides the driving force for the diffusion. He found that steel sheet 0.064 inch thick that contained 0.85 per cent carbon decarburized to 100 per cent ferrite in 15 hours at 1500 F in hydrogen that contained 20 per cent water vapor. He showed experimentally that copper plate allows no decarburization in 6 hours at 1550 F.

Buzzard and Cleaves(23) cited five references which indicate that oxygen apparently is readily removed from iron by hydrogen treatment, but a higher temperature is required than for the removal of carbon. As is the case with the removal of carbon, the moisture content of the hydrogen is an important factor in the reaction with oxygen. Apparently, oxygen removal is more effective if the iron is in the form of a finely divided aggregate or is molten. They also listed nine references indicating that treatment of steel with hydrogen at high temperatures removes nitrogen too, and other references suggest that such a treatment may remove phosphorus and sulfur.

HYDROGEN AT HIGH PRESSURES AND NORMAL TEMPERATURE

Hydrogen gas at high pressures (up to several thousand psi) can be handled safely in carbon-steel cylinders at ordinary temperatures, and such cylinders are specified by the Interstate Commerce Commission for safely transporting the gas.

The attack of steel by hydrogen at normal temperatures and very high pressure (8,700 atm, or 128,000 psi) has been reported by Bridgman(42,43). A hollow chromium-vanadium steel cylinder that contained hydrogen under pressure allowed the hydrogen to escape with explosive violence when the pressure reached 8,700 atm, but there was no visible damage to the cylinder. The same vessel previously withstood liquids at 25,000 atm without damage. However, if a similar vessel was pressurized with hydrogen several times, a visible crack slowly developed, and the steel was severely embrittled.

Poulter and Uffelman(44) constructed concentric cylinders, the inner one being a 1/8-inch-thick liner. This device withstood 20,000 atm of oil pressure without failure. On pressurizing the cylinders with ordinary molecular hydrogen, they observed rapid penetration of hydrogen through the steel at 6,000 atm (88,200 psi), but there was no such effect at a pressure of 4,000 atm (58,800 psi). However, when atomic hydrogen was generated by the action of sulfuric acid on zinc dust, a rapid evolution of hydrogen through the wall of the inner cylinder occurred after only 5 minutes at 4,000 atm, and the gas was followed by the penetration of a small quantity of the acid solution. Then the same cylinder was cleaned and pressurized with oil at 4,000-atm pressure. Some of the oil passed through the cylinder wall so that the pressure dropped to 500 atm (7,350 psi) in 2 hours. Subsequently, careful examination of the liner under a low-power microscope revealed no flaws. However, when it was filled with hydrogen at 100 psi (6.8 atm) and immersed in water, very small bubbles of hydrogen appeared all over the outer surface of the liner within about a minute.

The effect of hydrogen at very high pressures also is strikingly shown by the following illustration. Pressure vessels suitable for operation with oil at pressures in excess of 7,000 atm (103,000 psi) failed in a brittle manner with hydrogen at pressures as low as 2,000 atm (29,400 psi)(45). The solution to this particular problem was to use liners that were essentially impervious to the penetration of hydrogen at elevated pressures and room temperature. The bores of the steel vessels were provided with continuous, shallow, spiral grooves from end to end to prevent any hydrogen pressure buildup between the liner and the vessel. The most successful lining material tested was Type 316 austenitic stainless steel. The use of this material for periods up to several months was successful in eliminating brittle ruptures. Furthermore, bursting tests on stainless steel vessels pressurized with hydrogen resulted in failure at the same pressure as with oil.

Based on the published results of Bridgman and of Poulter and Uffelman, described above, and on the knowledge that various other investigators had studied the properties of hydrogen and hydrogen-containing gases at pressures of 3,000 atm and even 5,000 atm without observing any damage to their equipment, Dodge(46) believed that no serious trouble would ensue if hydrogen was compressed in an ordinary alloy-steel vessel to 3,000 atm. However, he and his co-workers were wrong in this belief. An intensifier which had been used repeatedly to pump oil at 4,000 atm and had been used several times to compress nitrogen to the same pressure, failed within a matter of minutes when used to compress hydrogen at not over 3,000 atm (44,100 psi). The failure consisted of very fine cracks that were barely visible to the naked eye, but easily seen when special techniques were used to develop them. They were large enough that the intensifier was completely useless, even for compressing oil. This led Dodge to conduct considerable work on the effect of high-pressure hydrogen, both at room temperature and at elevated temperatures, on a wide variety of materials.

The effects of very high pressures of hydrogen at room temperature on several steels and nickel-base alloys were investigated by Van Ness and Dodge(47). The compositions of the materials studied are listed in Table 4. This work was incomplete at the time the referenced report was published, tests having been made only under the following conditions:

13 hours at 2,000 atm
13 hours at 3,000 atm
18 hours at 4,000 atm
1 hour at 4,000 atm.

Only Nichrome, Incoloy, the austenitic Type 302 stainless steel and the two 400-series stainless steels were not affected by hydrogen under the conditions listed. However, subsequent tests showed that the two 400-series stainless steels were embrittled after exposures of several days. All the other materials showed some loss of ductility as a result of exposure to hydrogen at these high pressures. The last five materials listed are plain-carbon steels. Two of these, AISI 1010 and AISI 1095 proved to be susceptible to moderate embrittlement under the conditions investigated, and both to about the same extent, indicating that the large difference in carbon content was not important here. Representative results of bend tests of the other plain-carbon materials are given in Table 5. The aluminum-killed steel had a much higher resistance to embrittlement than did the other two materials. It was concluded that hydrogen pressures as low as 2,000 atm (30,000 psi) can cause dangerous embrittlement of steels even at room temperature.

These investigators experienced no trouble with hydrogen embrittlement of any of their equipment made of low-alloy steels at hydrogen pressures below 2,000 atm. Also, the materials used for equipment in contact with 4,000-atm hydrogen, that is, austenitic stainless steel and beryllium copper, proved to be satisfactory.

TABLE 4. MATERIALS USED IN A STUDY OF THE EFFECT OF VERY HIGH PRESSURES OF HYDROGEN AT ROOM TEMPERATURE(47)

Material	Composition, weight per cent						
	C	Fe	Cr	Ni	W	V	Other
Rex M-2 tool steel	0.83	Bal	4.15	--	6.4	1.9	5Mo
Rex AA tool steel	0.73	Bal	4.	--	18.	1.15	--
Commercially pure nickel	--	--	--	Bal	--	--	--
Monel metal	0.16	1.4	--	Bal	--	--	30Cu
Inconel	0.08	7.5	15.5	Bal	--	--	--
Inconel X	0.04	7.	15.	Bal	--	--	2.5Ti
Nichrome	0.06	Bal	16.	60.	--	--	--
Incoloy	0.07	Bal	21.	34.	--	--	--
Type 302 SS	0.11	Bal	17.76	8.74	--	--	--
Type 410 SS	0.072	Bal	13.12	--	--	--	--
Type 430 SS	0.08	Bal	17.65	0.12	--	--	--
Cold-rolled rimmed steel	0.08	Bal	--	--	--	--	--
Cold-rolled Al-killed steel	0.05	Bal	--	--	--	--	--
Cold-rolled Vitrenamel	0.03	Bal	--	--	--	--	--
AISI 1010 Steel	0.1	Bal	--	--	--	--	--
AISI 1095 Steel	0.95	Bal	--	--	--	--	--

TABLE 5. REPRESENTATIVE RESULTS OF BEND TESTS MADE ON MATERIALS EXPOSED TO HIGH-PRESSURE HYDROGEN AT ROOM TEMPERATURE(47)

	Bends Required for Failure		
Exposure	Rimmed Steel	Al-Killed Steel	Vitrenamel
None	56	70	54
13 hr at 2,000 atm	--	--	45
13 hr at 3,000 atm	39	30	43
18 hr at 4,000 atm	21	61	25
1 hr at 4,000 atm	51	79	44

Perlmutter and Dodge(48) exposed more than 50 metals to hydrogen between 7,500 and 60,000-psi pressure at room temperature. Included were five ferritic stainless steels, six special iron-chromium alloys with from 10 to 20 per cent chromium, and a group of 14 irons, plain-carbon steels, low-alloy steels, clad steels, and other ferrous alloys.

The mere presence of chromium did not provide protection against embrittlement by hydrogen. However, the results indicated that when it served to create a stable chromium oxide surface film, as in Types 430 and 321 stainless steel, chromium definitely improved the resistance of an alloy, depending on the pressure and the time of exposure. The induction period observed before embrittlement occurred in these stainless steels was presumed to be the time needed for hydrogen to penetrate the surface oxide film. For Type 430 stainless steel, this induction period increased with decreasing pressure until at pressures below 7,500 psi it exceeded 40 days. At 60,000-psi pressure, this time of protection was only 1 day, as is shown in Figure 7. In the Type 420 stainless steel with only 13 per cent chromium, the surface oxide film was less stable and embrittlement began to occur immediately upon exposure (see Figure 8).

Among the low-alloy steels and irons, alloy content alone did not control the resistance. Low-carbon AISI 1020 steel in the form of hot-rolled sheet could not be embrittled under extreme pressure for long periods. However, Armco iron samples were rapidly and quite severely affected, and were embrittled by exposure to hydrogen at only 1000-atm pressure. Vitrenamel and Puron, the other relatively pure irons tested, behaved like Armco iron. Besides the low-carbon steel, only the T-1 steel was completely unchanged by the hydrogen treatment. All other ferrous materials were embrittled to a greater or lesser extent. The embrittlement was particularly severe on the titanium steel, Maxel shank steel, Puron, Vitrenamel, and the coated steels (Nifer, Alfer, and galvanized iron). Nifer and Alfer are clad with nickel and aluminum, respectively. The behavior of Alfer was similar to that of Type 430 stainless steel, which the authors suggested was not surprising since it has a stable oxide outer film and a macroscopic layer of metallic aluminum over the steel. (Tests of aluminum showed no embrittlement.) For the length of time it took the hydrogen to penetrate to the steel, no embrittlement was recorded for Alfer, since the aluminum layer itself is not embrittled (see Figure 9). Conversely, nickel possesses neither an oxide film of the Al_2O_3 type, nor the resistance to embrittlement that aluminum has. Nifer began to show hydrogen embrittlement very soon after exposure, as is shown in Figure 10. Just as zinc and aluminum behaved similarly toward hydrogen, galvanised iron was similar to Alfer in behavior. Some of these results are listed in Table 6. These data show that greater hydrogen absorption and more severe hydrogen attack (with resultant increase in embrittlement) go hand in hand. Without exception, the amount of hydrogen evolved from the first group of samples by warm extraction under mercury was less than 0.1 relative volume. At the other extreme, badly attacked specimens all gave values of evolved hydrogen greater than 0.22 relative volume, and usually considerably more hydrogen was evolved.

Borelius and Lindblom(49) compared the rate of permeation of hydrogen through an iron diaphragm in two types of experiments. In one series of experiments, the rate was measured when the iron was exposed to hydrogen gas of different pressures. In the other experiment, hydrogen was delivered to the iron surface by electrolytic action in a 2N NaOH electrolyte. By extrapolation of their data, they indicated that the rate of permeation should be the same at ordinary temperatures for a gas pressure of 250 atm or a current density of 0.015 amp/cm^2 (0.097 amp/in.^{2}) with the indicated electrolyte.

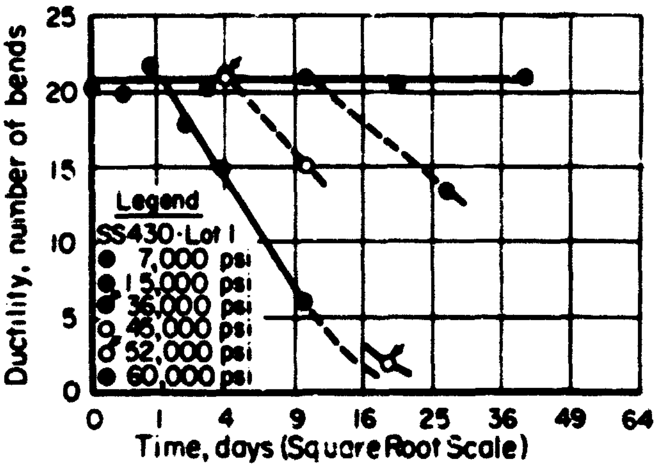


FIGURE 7. DUCTILITY OF TYPE 430 STAINLESS STEEL EXPOSED TO HYDROGEN GAS AT ROOM TEMPERATURE(48)

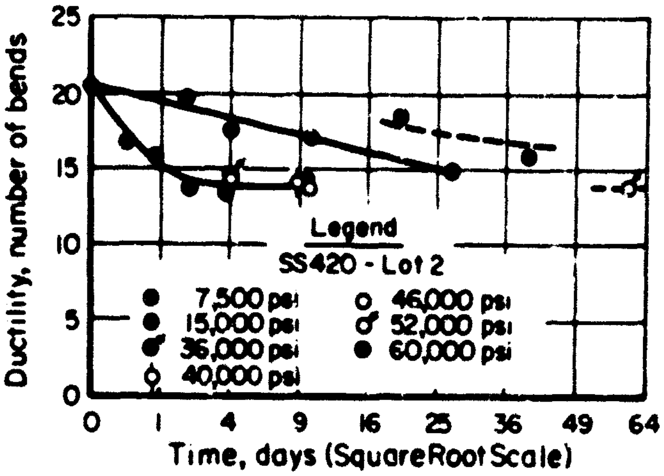


FIGURE 8. DUCTILITY OF TYPE 420 STAINLESS STEEL EXPOSED TO HYDROGEN GAS AT ROOM TEMPERATURE(48)

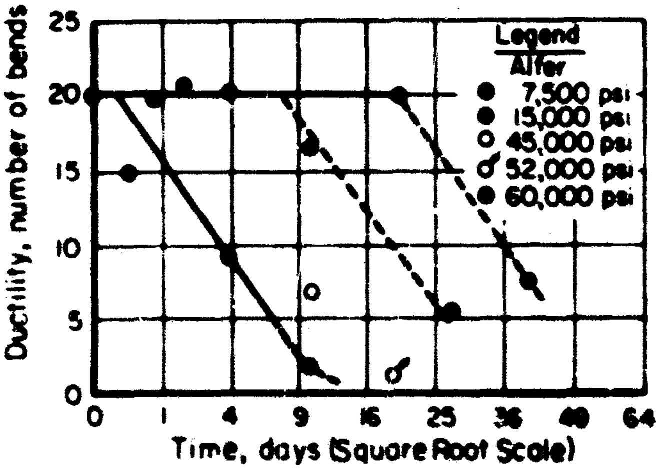


FIGURE 9. DUCTILITY OF ALFER EXPOSED TO HYDROGEN GAS AT ROOM TEMPERATURE(48)

Alfer is low-carbon steel clad on each side with Al-1 [illegible] cladding [illegible] 10 per cent on each side.

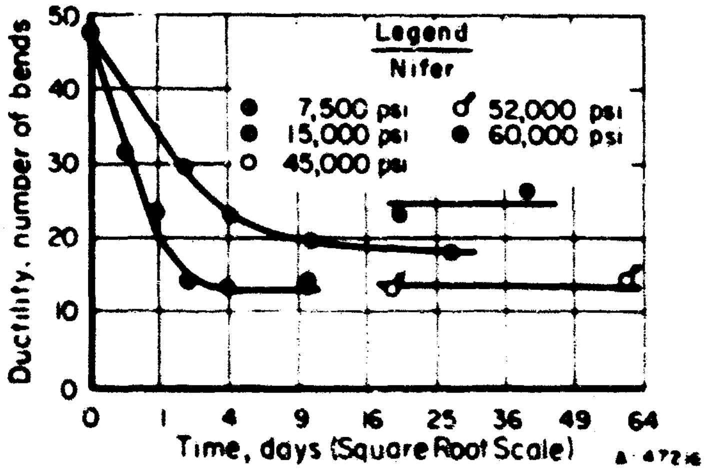


FIGURE 10. DUCTILITY OF NIFER EXPOSED TO HYDROGEN GAS AT ROOM TEMPERATURE(48)

Nifer is low-carbon steel clad on each side with grade [illegible] nickel; cladding thickness = 10 per cent on each surface.

TABLE 6. RELATIONSHIPS OBSERVED AMONG EXPOSURE TO HYDROGEN, THE AMOUNT OF HYDROGEN ABSORBED (INDICATED BY THE AMOUNT OF HYDROGEN EVOLVED BY WARM EXTRACTION UNDER MERCURY), AND THE RELATIVE DEGREE OF EMBRITTLEMENT FOR VARIOUS MATERIALS EXPOSED AS INDICATED(48)

Material	Conditions of Exposure	Gas: Metal Volume Ratio(a)
Not embrittled or only slightly embrittled;(b) less than 10% reduction in ductility and less than 30% of maximum reduction recorded		
Low-carbon steel(c)	Control, as received	0.015
Stainless steel 420	Control, as received	0.00
AISI 1020	2N H_2SO_4 acid, 6 hours, 70 C(d)	0.045
AISI 1020	7300-psi hydrogen, 40 days	0.055
Monel	6N HCl acid, 44 hours	0.090
Moderately embrittled; over 10% reduction in ductility and less than 50% of maximum reduction recorded		
Nifer(e)	60,000-psi hydrogen, 6 hours	1.2
Alfer(f)	60,000-psi hydrogen, 6 hours	4.4
Severely embrittled; over 10% reduction in ductility and over 50% of maximum reduction recorded		
Special alloy No. 3(g)	60,200-psi hydrogen, 9.7 days	0.22
AISI 1020	15N H_2SO_4 acid, 51 hours	0.22
Stainless steel 420	7300-psi hydrogen, 40 days	0.32
Nifer(e)	45,500-psi hydrogen, 10 days	0.38
Low-carbon steel	15N H_2SO_4 51 hours	0.62
Nichrome	52,200-psi hydrogen, 40 days	0.67
Nickel	58,600-psi hydrogen, 20 days	0.98
Alfer(f)	2N H_2SO_4 acid, 1 day	1.2
Galvanized iron	60,200-psi hydrogen, 9.7 days	1.2
Nickel	52,200-psi hydrogen, 40 days	1.5
Monel	14,700-psi hydrogen, 27 days	1.8

(a) The amount of hydrogen evolved was expressed as the ratio of hydrogen gas volume at standard temperature and pressure to the metal volume, that is, relative volumes.

(b) Embrittlement was based on the reduction in the number of 180-degree bends required to rupture the specimens exposed to hydrogen compared with the number for the corresponding nonhydrogenated specimens.

(c) 0.016C, 0.011Cu, 0.02Mn, 0.007Si, 0.005P, 0.021S.

(d) This run was made at 70 C (158 F); all others whether acid or gas exposure, were made at room temperature.

(e) Nifer is low-carbon steel clad on each side with Grade 330 nickel; cladding thickness was 10 per cent on each side.

(f) Alfer is low-carbon steel clad on each side with Al-1.2Si alloy; cladding thickness was 10 per cent on each side.

(g) Special alloy No. 3 was 80Fe-20Cr.

They suggested the following approximate relationship for the 2N NaOH electrolyte:

$$p\ (\text{atm}) = 17{,}000 \cdot (\text{amp/cm}^2)\ .$$

This relationship bears out the observations of other investigators that hydrogen can be introduced into steel by exposing steel to high-pressure hydrogen at room temperature, and also shows that high pressures are required to introduce hydrogen at a rate that is readily achieved by cathodic charging at relatively low current densities.

The rate of permeation of hydrogen in an occluding cathode is affected by the hydrogen-ion concentration of the electrolyte for corresponding current densities. Therefore, for a highly ionized acid electrolyte, a pressure equivalent several times as great as indicated above probably would be obtained.

Poulter(50) described a 200-cubic-foot hydrogen cylinder which failed in a brittle manner after being in service for about 25 years. A careful examination of this cylinder showed that the inside surface was covered with small cracks, some of which extended as much as 25 per cent of the way through the cylinder wall. Hydrogen cylinders were then selected that had been in service about the same length of time, but which had not failed. Examination showed the inside surfaces to be in approximately the same condition as the one that failed, whereas, cylinders made at the same time and from the same lot of steel, but which had been in nitrogen service, were uncracked.

HYDROGEN AT ELEVATED TEMPERATURES AND PRESSURES

Exposure to Hydrogen-Nitrogen Mixtures

Beginning in 1908 with the development of the Haber synthetic-ammonia process, the first important process in which hydrogen was used at high temperatures and pressures, attack by hydrogen of the materials from which the equipment was constructed has been a problem. Since that time, processes for the hydrogenation of coal, tars, or petroleum, to produce liquid fuel, and a number of synthetic hydrocarbon processes that involve hydrogen or dehydrogenation have been developed. Hydrogen at high temperatures and pressures can be insidiously destructive to metals, including many steels, and this can occur without visible thinning of the part or readily observable changes in the appearance of the exposed surface. The problem is serious because the metal may develop many microscopic fissures, its strength may be reduced to very low values, and equipment operating under high pressure may suddenly burst without warning.

It was not until 1933 that Bosch described the difficulties encountered in his first attempts with Haber to synthesize ammonia from its elements under pressure and high temperature. An experimental vessel built in 1908 from carbon steel cracked after only 80 hours of service; it had a wall thickness of 30 mm (1.18 inches). After some experimentation, Bosch and Haber concluded that it was hydrogen and not nitrogen that was responsible for the deterioration of the steel. In 1911, satisfactory results were obtained with chromium steel, and this led to industrial application of the process in Germany in 1916.

These early German experiments with the nitrogen-fixation process of forming ammonia from the gaseous elements, hydrogen and nitrogen, showed that carbon steels were badly attacked during relatively short exposure to hydrogen-nitrogen mixtures at high temperatures and pressures. However, increased resistance to hydrogen attack was obtained by adding chromium, tungsten, molybdenum, or vanadium to the steel, either singly or in combination.

The damage caused by hydrogen at elevated temperatures and pressures is generally considered to be caused by hydrogen permeating the steel and reacting to form other gases. Of primary importance is the reaction of hydrogen with iron carbide to form methane. It is generally accepted that, once formed, methane cannot diffuse out of the steel. Continued reaction causes methane to accumulate within the steel and to build up high localized pressures which finally crack or blister the metal. Also, the loss of carbon weakens the steel so that it is less able to withstand these internal gas pressures or the applied stresses.

The introduction into the United States of the nitrogen-fixation process for the production of ammonia brought attention to the lack of information on the effects of gas mixtures at elevated temperatures and pressures on metals. The plain-carbon steels used to contain the gases were quite susceptible to deterioration, and failures were experienced, just as had been encountered by the Germans. Knowing that the Germans had solved the problem by using alloy steels, the U. S. company developing the process made several small bottles from forged and from cast steels of different compositions and kept them filled with the synthesis gas mixture at process conditions (1500 psi and 930 to 1110 F) until they failed(51). The time to failure varied considerably, being a few days for a plain-carbon steel casting; 4 to 6 months for a plain-carbon steel forging, a nickel-steel forging, and a chromium-steel forging; and more than 2 years for a forging of chromium-vanadium steel. The chromium-vanadium steel (0. 30C, 1. 0Cr, 0. 18V) that offered improved resistance was used in production up to the time of Vanick's investigations, which comprised the first major study of hydrogen attack in the synthesis of ammonia.

Vanick(52) first studied the effect of exposure to reducing gas mixtures of hydrogen, nitrogen, and ammonia on commercially pure iron, nickel, and copper and on a large number of their alloys. Samples in the form of corrosion specimens, tensile specimens, and pressure bombs were exposed to a synthesizing ammonia-gas mixture (3 volumes of hydrogen to 1 volume of nitrogen, plus a few per cent ammonia) at a temperature of 500 C (930 F) and a pressure of 100 atm (1500 psi) for as long as 6 months. In addition, short exposures were made to ammonia-rich "cracking ammonia". None of the materials tested, except those exposed to decomposing ammonia (cracking ammonia), were corroded in the sense of undergoing visible surface attack accompanied by surface disintegration or formation of chemical compounds. Nearly all the materials suffered deterioration as measured by loss in tensile strength and ductility. Iron-base alloys containing chromium, nickel, and aluminum seemed to offer the most resistance to hydrogen attack under service conditions requiring the ability to sustain stress at elevated temperatures and pressures*.

In subsequent work, Vanick(53) experimented with 10 commercial steels, mostly forging steels of the compositions shown in Table 7. The steels were double annealed

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*Other investigators since have shown that nickel steels do not offer improved resistance to hydrogen attack as compared with plain-carbon steels.

for stress relief. They were exposed to a $3H_2:1N_2$ gas mixture containing 8.3 per cent NH_3 at 930 F and 100-atm pressure for 4 months. The results of the tests of bombs and specimens, listed in Table 8, showed that (1) the carbon content should be kept low, (2) increasing the chromium content was helpful, and (3) tungsten was a useful addition, the chromium-tungsten steel being the least affected in this group of 10 steels.

TABLE 7. COMPOSITIONS OF 10 COMMERCIAL STEELS EXPOSED TO A HYDROGEN-CONTAINING GAS MIXTURE FOR 4 MONTHS$^{(53)}$

Steel	SAE	Composition, per cent								
No.	Designation	C	Mn	P	S	Si	Cr	Ni	V	W
31	1020	0.19	0.43	0.008	0.033	0.17	....	....	....	....
32	1095	1.01	0.40	0.007	0.036	0.16	....	....	....	....
33	2330	0.24	0.52	0.008	0.032	0.03	....	3.43	....	....
34	6130	0.30	0.68	0.012	0.024	0.26	0.93	....	0.18	....
35	3335	0.39	0.70	0.011	0.044	0.29	0.84	3.56	....	....
36	3230	0.27	0.59	0.014	0.022	0.13	1.00	1.60	....	....
37	52100	0.93	0.30	0.010	0.014	0.21	1.47	....	....	....
38	5140	0.48	0.79	0.030	0.029	0.23	0.60	....	....	....
39	7260	0.58	0.36	0.004	0.017	....	0.55	0.21	....	1.62
40	2512	0.10	0.31	0.008	0.023	0.31	....	4.87	....	....

TABLE 8. EFFECT OF 4 MONTHS' EXPOSURE TO A HYDROGEN-NITROGEN-AMMONIA MIXTURE AT 930 F AND 100-ATM PRESSURE ON THE STRENGTH OF THE STEELS LISTED IN TABLE 7$^{(53)}$

	Percentage of Original Tensile Strength Retained		Percentage of	Loss of Strength
Steel No.	Bomb Walls (A)	Tensile Specimen (B)	Thickness of Bomb Wall Affected (C)	per Unit of Affected Area, $\frac{100-A}{C}$
31	105.0	76.0	18.0	....
32	18.7	32.7	73.5	1.105
33	81.0	71.0	49.7	0.383
34	86.0	65.7	9.6	1.46
35	69.6	44.4	10.9	3.59
36	84.5	59.4	8.7	1.78
37	47.7	36.9	17.0	3.08
38	65.1	54.3	27.8	1.255
39	96.3	89.8	None	....
40	95.8	91.3	42.9	0.098

For the chromium steels (neglecting the Cr-W steel), the greatest resistance to penetration occurred in the order of increasing chromium/carbon ratio, regardless of the presence of other elements. This is shown as follows:

Steel	Cr/C Ratio	Relative Order of Resistance to Penetration[(a)]
36	3.7	1
34	3.1	2
35	2.15	3
37	1.58	4

(a) 1 = most resistant, etc.

A second experiment was performed on a series of Cr-V steels in which the carbon content was varied from 0 to 1.15 per cent, chromium from 0 to 14 per cent, and vanadium from 0 to 0.65 per cent. The compositions are shown in Table 9. After double

TABLE 9. COMPOSITIONS OF 14 CHROMIUM-VANADIUM STEELS EXPOSED TO A HYDROGEN-CONTAINING GAS MIXTURE FOR 10 MONTHS (53)

Steel No.	Composition, per cent						
	C	Mn	P	S	Si	Cr	V
				Chromium Series			
1	0.37	0.39	0.017	0.022	0.27	0.04	0.19
2	0.29	0.53	0.015	0.011	0.16	0.51	0.28
3	0.30	0.68	0.012	0.024	0.26	0.93	0.18
4	0.31	0.48	0.011	0.011	0.12	2.01	0.34
5	0.33	0.37	0.028	0.013	0.26	7.70	0.18
6	0.42	0.35	0.025	0.009	0.06	14.40	0.18
				Vanadium Series			
7	0.40	0.53	0.018	0.013	0.18	1.05	0.02
8	0.37	0.52	0.018	0.018	0.20	1.05	0.07
9	0.35	0.37	0.020	0.013	0.20	1.02	0.14
10	0.37	0.55	0.018	0.019	0.18	1.07	0.31
11	0.27	0.34	0.025	0.011	0.29	1.24	0.65
				Carbon Series			
12	0.16	0.55	0.023	0.023	0.34	1.03	0.20
13	0.58	0.68	0.011	0.017	0.23	0.73	0.18
14	1.16	0.55	0.022	0.018	0.20	1.06	0.20
				"Stainless" Steels			
27	0.25	0.40	0.020	0.020	0.60	13.50	....
28	0.48	0.09	0.018	0.014	0.43	21.10	0.07

annealing for stress relief, the steels were made into both bombs and specimens; these were exposed for 10 months under the same conditions that were used for the first series. The data in Table 10 and other results obtained in this investigation showed that (1) a low carbon content was desirable, (2) vanadium gave some improvement in resistance to attack, and (3) 2.0 per cent chromium stopped selective penetration and intergranular fissuring and slowed the rate of penetration under the conditions of this investigation. The rate of penetration is shown in Figure 11. Note the high resistance of the stainless steels (Steels 6, 27, and 28) and the 7.7 and 2.0 per cent chromium steels (Steels 5 and 4, respectively). Larger quantities of chromium (greater than 2.0 per cent) further improved resistance to attack, but not in proportion to the amount of chromium. The straight-chromium and the chromium-nickel stainless steels were the most resistant, but they are more difficult to forge and machine and are more expensive.

TABLE 10. EFFECT OF 10 MONTHS' EXPOSURE TO A HYDROGEN-NITROGEN-AMMONIA MIXTURE AT 930 F AND 100-ATM PRESSURE ON THE STRENGTH OF THE CHROMIUM-VANADIUM STEELS LISTED IN TABLE 9(53)

Steel No.	Percentage of Original Tensile Strength Retained: Bomb Walls (A)	Percentage of Original Tensile Strength Retained: Tensile Specimen (B)	Percentage of Thickness of Bomb Wall Affected (Fissured) (C)	Loss of Strength per Unit of Affected Area, $\frac{100-A}{C}$ (D)
		Chromium Series		
1	81	86.5	31	0.62
2	80	79.0	38	0.53
3	70	66.0	23	1.32
4	59.5	67.0	13	3.24
5	93	62.0	6	1.27
6	97.5	....	0	....
		Vanadium Series		
7	66.5	51.5	30	1.13
8	72.5	61	44	0.62
9	73	44	63	0.42
3	70	66	23	1.32
10	79	44	22-71	0.94-0.29
11	95	71.5	21-84	0.24-0.06
		Carbon Series		
12	81	91	34	0.56
3	70	66	23	1.32
13	59	49	53	0.77
14	78	72	42	0.56

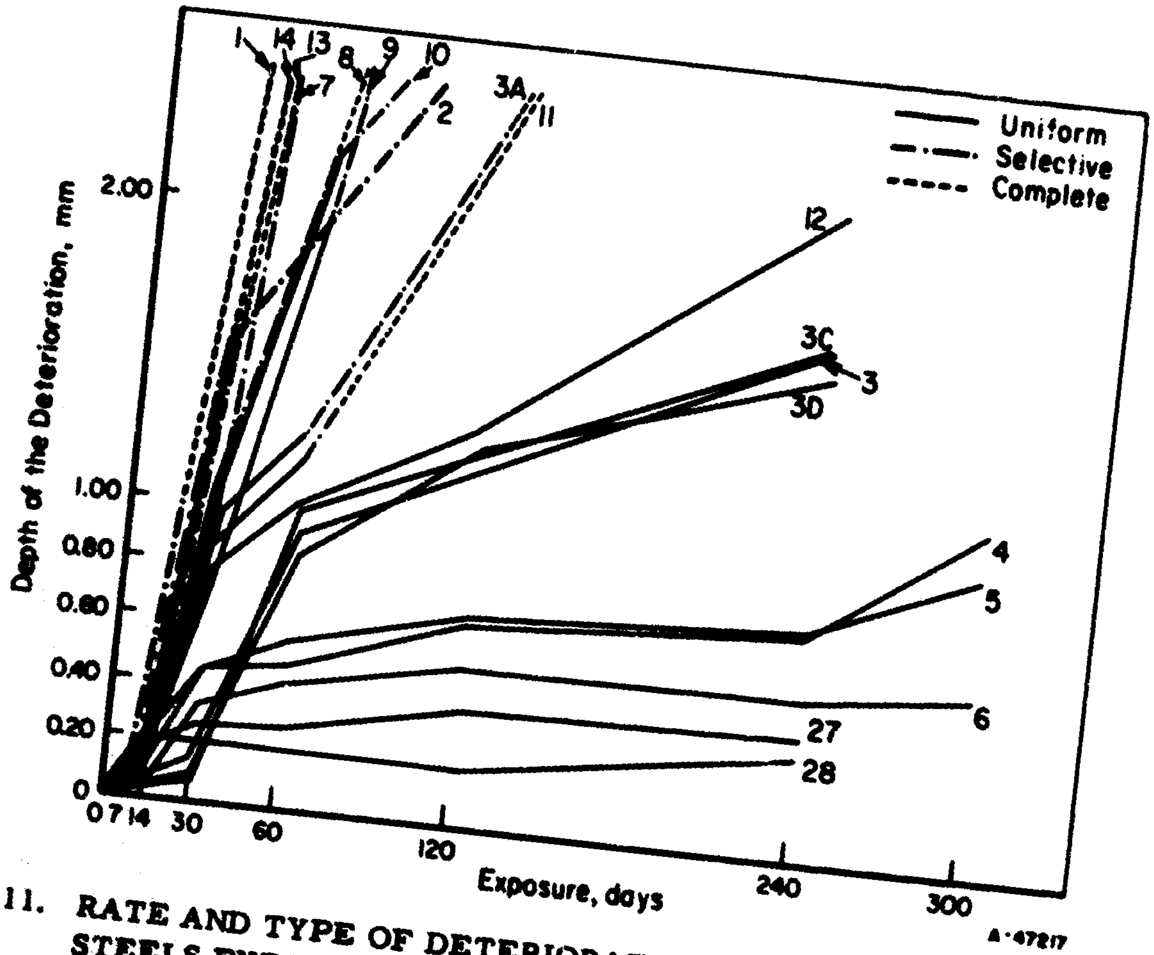

FIGURE 11. RATE AND TYPE OF DETERIORATION OF CHROMIUM-VANADIUM STEELS EXPOSED TO A HYDROGEN-NITROGEN-AMMONIA MIXTURE AT 930 F AND 100-ATM PRESSURE(53)

Numbers refer to steels listed in Tables 9 and 10.

The progress of attack on the steels was marked by loss in strength and ductility, the occurrence of decarburization, and the development of fissures. Analyses for carbon of some of the exposed steels confirmed the microscopic evidence of decarburization. The following are typical results:

Steel	Condition	Carbon Content, per cent
38	Original	0.48
38	After 4 months' exposure	0.04
Cr-V	Original	0.34
Cr-V	After 6 months' exposure	0.07

Thus, the work of Vanick and co-workers at Fertilizer and Fixed Nitrogen Investigations in Washington, D. C., showed that a steel containing 2 per cent chromium satisfactorily resisted the potential corrosive attack and decarburization of a gas mixture of hydrogen, nitrogen, and ammonia at 500 C (930 F) and a pressure 100 atm. As a result of this work, a chromium-vanadium steel (about 0.30C, 2.0Cr, and 0.20V) apparently was used exclusively for the catalyst chambers for ammonia synthesis in this country for several years (at least up to 1933).(54) Vanick and co-workers also showed that a tungsten-bearing steel was exceptionally resistant(53,55). In a continuation of this work, Kosting(56) exposed a series of chromium-tungsten steels for 1 year to 3:1 hydrogen:nitrogen mixture with 10 per cent ammonia at a temperature of 300 C (570 F) and a pressure of 600 atm. Both premachined tensile specimens and hollow cylinders, or bombs, subjected to internal pressure were used. Table 11 shows the compositions of the forged steels investigated.

TABLE 11. CHEMICAL COMPOSITION OF CHROMIUM-TUNGSTEN STEELS USED IN A STUDY OF THE EFFECT OF AMMONIA SYNTHESIS GAS(56)

Identification	Composition, per cent						
	C	Mn	Si	Cr	W	V	Ni
1-382	0.36	0.50	0.24	--	0.81	--	--
2-386	0.33	0.41	0.19	0.20	2.85	--	--
3-387	0.38	0.46	0.14	--	4.40	--	--
4-388	0.32	0.49	0.16	--	7.25	--	--
5-417	0.35	0.50	0.08	--	11.69	--	--
6-CRV-6	0.3-0.4	--	--	1.00	--	0.07	--
7-390	0.34	0.44	0.21	1.00	1.15	--	--
8-391	0.37	0.50	0.26	1.06	3.30	--	--
9-392	0.33	0.33	0.23	1.04	5.25	--	--
10-399	0.33	0.43	0.28	2.42	--	0.20	--
11-460	0.40	0.56	0.23	2.67	--	--	--
12-393	0.32	0.46	0.24	2.44	1.05	--	--
13-394	0.33	0.47	0.19	2.49	3.20	--	--
14-396	0.34	0.43	0.14	2.45	5.15	--	--
15-395	0.12	0.44	0.12	1.01	3.10	--	--
16-397	0.57	0.47	0.15	1.04	2.93	--	--
17-433	0.93	0.60	0.22	1.12	2.94	--	--
18-459	0.29	0.65	0.24	2.20	--	--	29.35
19(a)	0.3-0.4	--	--	1.9-2.1	--	0.18-0.20	--

(a) Replacement for Bomb 17.

The alloy with 0.81 per cent tungsten and no chromium suffered the greatest loss in tensile properties. By increasing the tungsten to 2.85 per cent, attack was prevented under the selected test conditions. However, further tungsten additions offered no additional benefit, and adding as much as 11.69 per cent tungsten was detrimental. Chromium was a more effective alloy addition, 1 per cent being sufficient to impart resistance to deterioration for 1 year under the conditions used. No improvement was found by adding tungsten to the chromium steels, but the addition of chromium to the tungsten steels was very beneficial. There were indications that the higher the tungsten content, the greater the amount of chromium that was required. The upper limit for carbon content for the conditions of these experiments was 0.35 per cent. Lowering the carbon gave better resistance to hydrogen attack, but with a sacrifice in the initial strength of the alloy.

The changes in properties of these steels are given in Table 12. The way the alloys are grouped, the effects of chromium and tungsten are shown clearly. Only the 0.81W alloy showed serious decarburization and serious loss of properties. This steel, in 1 year, lost 42 per cent of its tensile strength, 98 per cent of its reduction in area, and 82 per cent of the elongation over a 1-1/2-inch gage length.

Slag present at any exposed surface was attacked and decomposed, resulting in pitting.

TABLE 12. CHANGE IN ROOM-TEMPERATURE TENSILE PROPERTIES OF STEELS EXPOSED FOR 1 YEAR TO $3H_2:1N_2$ GAS MIXTURE CONTAINING 10 PER CENT AMMONIA AT 570 F AND A PRESSURE OF 600 ATM, SHOWING THE RESISTANCE IMPARTED BY VARIOUS ADDITIONS OF CHROMIUM AND TUNGSTEN(56)

			Change in Properties							
Constant Element	Increasing Element	Group No.	Tensile Strength, psi	Change, per cent	Yield Point, psi	Change, per cent	Reduction in Area, per cent	Change, per cent	Elongation, per cent	Change, per cent
0% Cr	W	1	-34,600	-42	-10,800	-26	-30.8	-98	-18.8	-82
		2	-600	-0.7	-13,700	-25	-4.2	-10	+2.1	+9
		3	-1,900	-2	-13,300	-23	-4.8	-12	--	--
		4	-1,800	-2	-13,200	-22	-1.1	-2	+2.5	+12
		5	-4,500	-4	-17,500	-27	-14.3	-31	-5.9	-29
1% Cr	W	6	0	0	+4,900	+11	-0.4	-0.7	+ 2.1	+6
		7	+1,000	+1	-10,300	-25	+11.8	+55	+4.1	+32
		8	0	0	-7,800	-14	-3.7	-8	-2.1	-8
		9	+500	+0.5	-15,600	-23	-0.7	-1	-6.7	-25
2-1/4% Cr	W	10	-1,100	-1	-4,900	-11	-0.9	-2	0	0
		11	+1,600	+1	+900	+2	-4.3	-11	-4.5	-24
		12	-500	-0.5	-12,600	-21	-2.3	-7	0	0
		13	-300	-0.3	+6,400	+13	-8.6	-17	-4.2	-16
		14	-900	-0.9	-6,800	-12	+2.7	+5	0	0
1% Cr-3% W	C	15	-1,200	-2	+3,900	+11	-0.4	-0.7	-2.0	-6
		8	0	0	-7,800	-14	-3.7	-8	-2.1	-8
		16	-1,000	-0.8	-1,000	-2	-46.0	-66	-3.6	-19
		17	-3,300	-2	-17,600	-20	-0.5	-10	--	--
2% Cr-30% Ni	--	18	+10,000	+12	-7,800	-19	-7.9	-14	-4.2	-9
0% W	Cr	6	0	0	+4,900	+11	-0.4	-0.7	+2.1	+6
		10	-1,100	-1	-4,900	-11	-0.9	-2	0	0
		11	+1,600	+1	+900	+2	-4.3	-11	-4.5	-24
1% W	Cr	1	-34,600	-42	-10,800	-26	-30.8	-98	-18.8	-82
		7	+1,000	+1	-10,300	-25	+11.8	+55	+4.1	+32
		12	-500	-0.5	-12,600	-21	-2.3	-7	0	0
3% W	Cr	2	-600	-0.7	-13,700	-25	-4.2	-10	+2.1	+9
		8	0	0	-7,800	-14	-3.7	-8	-2.1	-8
		13	-300	-0.3	+6,400	+13	-8.6	-17	-4.2	-16
5% W	Cr	3	-1,900	-2	-13,300	-23	-4.8	-12	--	--
		9	+500	+0.5	-15,600	-23	-0.7	-1	-6.7	-25
		14	-900	-0.9	-6,800	-12	+2.7	+5	0	0

Cox(54) discussed a private communication that dealt with the results of German work in which steels were exposed to a hydrogen-nitrogen mixture at 450 C (840 F) and 300-atm pressure for 630 hours. A Cr-V-Mo steel of very low carbon content (approximate composition 0.06C, 5Cr, 0.75Al, 0.05V, 0.40Mo) was hardly affected by exposure under these conditions.

The room-temperature mechanical properties of a number of SAE steels after exposure to $3H_2:1N_2$ ammonia synthesis mixture at 500 C (930 F) and 15,000 psi-pressure are shown in Figure 12. Maxwell(57) obtained these results on exposed test bars. They show the marked difference between the severely embrittled plain-carbon, nickel, and low-chromium steels on the one hand, and the more resistant higher chromium and chromium-molybdenum steels on the other hand. Maxwell found that chromium-tungsten and chromium-vanadium steels also offered improved resistance to hydrogen attack under the same conditions of exposure.

Ihrig(58) also studied the attack of 3:1 hydrogen-nitrogen ammonia synthesis mixture on a variety of steels; however, the conditions he used were more severe than had been used in the principal investigations conducted previously with this environment. He used pressures of 13,000 to 15,000 psi and temperatures up to 593 C (1100 F). The results of his investigation indicated that carbide-forming elements added to steels of intermediate chromium content do not prevent attack as previous investigators working at lower pressures had reported. He found blisters, decarburization, and fissures in such steels. Also, the more carbon the steels contained originally, the more severely were they attacked. Ihrig concluded that the austenitic Cr-Ni stainless steels, such as Type 317 (3.0Mo), Type 321 (0.46Ti), and Type 347 (0.78Cb), were the best to use at high pressures of hydrogen and nitrogen. However, since high-nitrogen layers were formed on their surfaces, he recommended that care be used in the design of high-pressure vessels, even when using these steels. Further, he recommended sampling the steel after various periods of operation to determine whether attack has been progressive.

Maxwell(57) also studied high chromium-nickel steels that contained from 12 to 36 per cent nickel and up to 25 per cent chromium. The seven alloys used were as follows:

	Approximate Composition, per cent			
Alloy	Cr	Ni	C	Other
ATV-1	11	36	0.30	
NCT	25	20	0.15	1.0Si
Midvale 25-20	25	20	0.18	
ATV-3	14	26	0.4	3.5W
Uniloy No. 2	21	12	0.2	1.0Cu, 1.5Si
Rezistal 2600	8	22	0.4	1.5Si
17A	8	20	0.4	

Test bars of these materials were exposed to $3H_2:1N_2$ ammonia-synthesis mixture at 500 C (930 F) and 1000-atm (15,000-psi) pressure for times up to 1535 hours. The results are summarized in Figure 13. He reported that the differences in the metal test bars after exposure were greater than might be expected from the curves in Figure 13. There was evidence of the beginning of surface attack on some which would have undoubtedly led to a break in the curve, if the test could have been continued longer. These

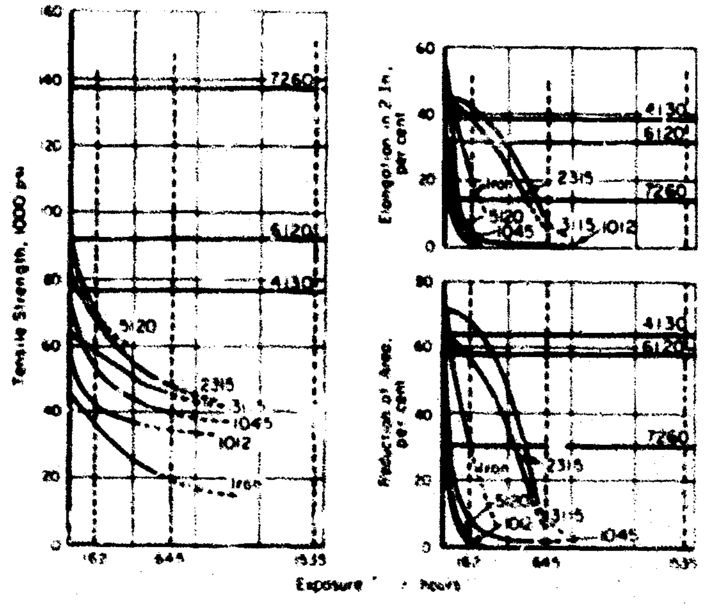

FIGURE 12. ROOM-TEMPERATURE MECHANICAL PROPERTIES OF SAE STEELS AND IRON AFTER EXPOSURE TO $3H_2$:$1N_2$ AMMONIA-SYNTHESIS MIXTURE AT 930 F AND 15,000-PSI PRESSURE(57)

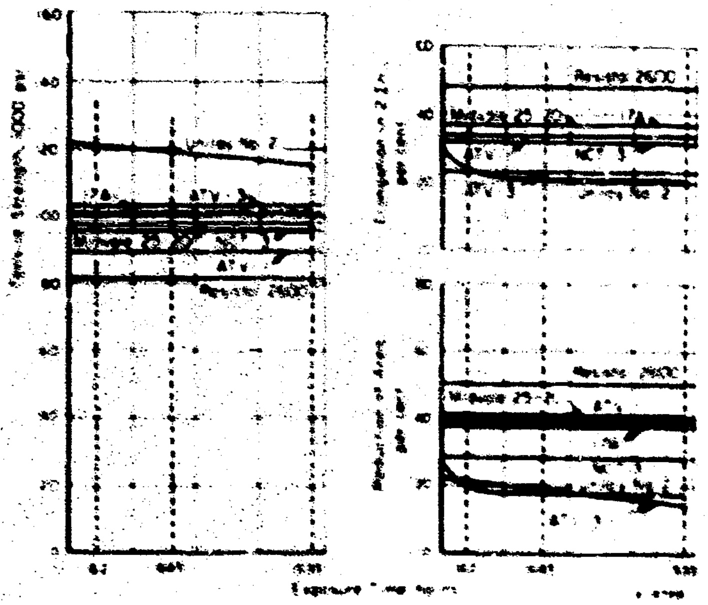

FIGURE 13. ROOM-TEMPERATURE MECHANICAL PROPERTIES OF HIGH NICKEL-CHROMIUM FERROUS ALLOYS AFTER EXPOSURE TO $3H_2$:$1N_2$ AMMONIA-SYNTHESIS MIXTURE AT 930 F AND 15,000-PSI PRESSURE(57)

results indicated that the majority of these high chromium-nickel steels are quite resistant to hydrogen-nitrogen attack. A test period of 5000 hours was suggested to show differences among the better steels of this group of seven.

Maxwell reported that 18-8 austenitic stainless steel had not consistently given satisfactory resistance in laboratory investigations under the conditions involved in the ammonia-synthesis process.* He implied that the unsatisfactory behavior of certain specimens was the result of free carbides present in the structure; however, details of the heat treatment and carbon contents were not reported. Maxwell expressed the opinion that the small added expense of using the more resistant 25Cr-20Ni or 25Cr-12Ni types was justified. The results of several other investigations indicated that 18-8 stainless steel is quite resistant to hydrogen attack under ammonia-synthesizing conditions.

Plant experiences derived from a synthetic-ammonia process have been summarized by Schuyten(59). The synthetic-ammonia process involved 3 to 1 hydrogen-nitrogen mixtures with 1 or 10 per cent ammonia at pressures of 1600 to 2000 psi and temperatures up to 475 C (885 F). Under these conditions, coarse-grained carbon steels with a structure consisting of ferrite and pearlite were attacked slightly at temperatures as low as 200 to 250 C (390 to 480 F) after exposures of 5 to 10 years. Carbon steels generally were found to show marked hydrogen attack at temperatures above 300 C (570 F). Low-carbon 0.5Cr-0.25Mo steel was found to be satisfactory to 300 C (570 F), and 0.30C-1.0Cr-0.25Mo steel in the normalized-and-tempered condition was resistant to 400 C (750 F). A 1.5Cr-0.5Mo steel with 0.30 per cent carbon, used for pressure vessels and forged fittings, was satisfactory at 450 C (840 F) in the normalized-and-tempered condition. A low-carbon 2.5Cr-0.5Mo steel was chosen for high-pressure tubing and heat-exchanger tubing. This steel was resistant to hydrogen attack under the most severe conditions encountered with this process at the plant described. A superficial nitrided case was formed at 420 to 450 C (790 to 840 F) owing to the dissociation of ammonia and the stability of the nitrides of chromium and molybdenum; however, it was reported that the depth of the case was limited and it did not affect the service life of the tubing. Straight-chromium and chromium-nickel stainless steels exhibited excellent resistance to hydrogen attack, but developed superficial nitrided cases. However, in addition, the chromium-nickel austenitic stainless steels were quite susceptible to room-temperature embrittlement, purportedly because of absorbed hydrogen which could be removed by a suitable annealing treatment.

The depth of attack appeared to increase with time in approximately linear fashion for the carbon steels, but with the chromium-molybdenum steels the depth of attack increased rather sharply at first and then appeared to reach a limiting value.

For the alloy steels, a very fine pearlitic or possibly bainitic structure, produced, for example, by normalizing followed by tempering, was considerably more resistant to hydrogen attack than was a structure in which the pearlite was coarser. Also, fine-grained structures were more resistant than were coarse-grained structures and for that reason, grain coarsening in the heat-affected zone of a weld may cause an otherwise resistant material to be susceptible to hydrogen attack. Under the most severe conditions experienced in the ammonia-synthesis plant described, oxide and sulfide inclusions in the steel, as well as the carbides, were reduced by hydrogen.

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*See Jones' discussion at the end of Reference 5[illegible] and Maxwell's reply.

In the ammonia-synthesis plant, attempts were made to protect carbon-steel welds from attack by overlays of resistant 18-8 stainless steel. However, this procedure was ineffective, because hydrogen readily diffused through the stainless steel layer and attacked the underlying carbon steel.

Substantial differences in resistance were observed between pressure-vessel walls and items of completely enclosed equipment. In the case of pressure vessels operating under conditions which resulted in a large temperature gradient through the walls (the outer surface being the colder), less attack was observed on the walls than on equipment which was entirely at the higher (process) temperature. Schuyten attributed these differences to the existence of temperature gradients and reduced opportunities for diffusion in the case of pressure-vessel walls. However, even at temperatures as low as 350 or 400 F, the diffusion of hydrogen in steel is quite rapid. Therefore, considering the long periods of exposure, reduced diffusion rates could hardly account for the observed differences. The reduced extent of attack apparently was the result of increased resistance to attack by hydrogen as the temperature was lowered.

Exposure to Hydrogen

Inglis and Andrews(60) studied the effects of hydrogen at 200 to 250-atm pressure and various temperatures between 150 and 500 C (300 and 930 F) on a number of steels. Table 13 lists the compositions of the steels investigated. The plain-carbon steels were tested in various conditions of heat treatment; the five alloy steels were tested in the hardened-and-tempered condition. Most of the tests consisted of passing hydrogen at the required pressure through heated tubes of the steel under test. Tests were carried out for times up to 5 years. Their results were as follows:

(1) At high pressures, hydrogen will attack steel at much lower temperatures than it will at normal pressure.

(2) In the first stage of the attack, the steel absorbs hydrogen and becomes embrittled, even though no decarburization or disintegration has occurred. At this stage, the original ductility can be restored by a suitable heat treatment to drive off the hydrogen. In the later stages of attack, the steel becomes decarburized and fissured, with consequent very severe loss in strength and ductility.

(3) The factors which determine the degree of attack are

  (a) Temperature
  (b) Pressure
  (c) Stress
  (d) Composition of the steel
  (e) Structure of the steel.

(4) For a given steel composition, the critical conditions giving rise to attack vary according to the structural condition of the steel, which is controlled by the heat treatment. The best structural condition is one in which the grain size is small; and, in general, the hardened-and-tempered condition is recommended.

(5) The limiting temperature giving rise to attack on mild steel may vary by 50 to 100 C (90 to 180 F), depending on the precise structural condition. A large thick-walled vessel, in which the desired structure cannot be attained, may be attacked at temperatures as low as 200 C (390 F), but smaller vessels of the same steel can be heat treated to give satisfactory resistance at that temperature.

(6) The commonly used engineering alloy steels, such as Ni-Cr, Ni-Cr-Mo Cr-V, Cr-Mo, etc., (but not straight-nickel steels) have resistance superior to that of mild steel. Also, with these alloy steels, the difference in structure between large and small vessels, after heat treatment, is much less than with mild steels. In the properly heat-treated condition, the limiting temperature at which attack of these steels will occur at 250-atm hydrogen pressure is between 300 and 350 C (570 and 660 F).

(7) In connection with the limiting temperatures causing attack, the effect of variations in the microstructure throughout a given tube or vessel must be considered. For example, they found that even a light sealing weld may alter the structural condition of the steel in the immediate neighborhood of the weld to such an extent that hydrogen attack will occur there under conditions that do not cause attack of the remainder of the steel. It may be necessary, therefore, to heat treat such parts after welding.

(8) Additions of chromium to steel progressively improve the resistance to hydrogen attack. Thus, at 250 atm, a 3 per cent chromium steel was resistant at temperatures up to 400 C (750 F), but was attacked appreciably at 450 C (840 F). On the other hand, a 6 per cent chromium steel was resistant up to at least 500 C (930 F).

(9) Austenitic chromium-nickel steels were not disintegrated by hydrogen at 250 atm and temperatures up to 450 C (840 F) for times up to 7,900 hours, but these steels suffered severe embrittlement. They absorbed large quantities of hydrogen under these conditions (3.8 cc/cc of steel for material tested at 450 C for 7,900 hours), and a very heavy carbide precipitation occurred at the grain boundaries. The ductility could be restored by a short-time heat treatment at high temperatures which the authors presumed could not have dissolved the grain-boundary carbides; therefore, they concluded that the loss of ductility resulted from the absorption of hydrogen which presumably was driven off by the recovery heat treatments.

TABLE 13. COMPOSITION OF STEELS USED BY INGLIS AND ANDREWS TO STUDY HYDROGEN ATTACK AS A FUNCTION OF TEMPERATURE AND PRESSURE(60)

Steel Number	Type of Steel	Composition, per cent					
		C	Cr	Ni	Mo	V	Si
1	Mild steel	0.12	--	--	--	--	0.07
2	Mild steel	0.12	--	--	-	--	0.01
3	Ni-Cr-Mo	0.28	0.70	3.38	0.38	--	0.21
4	Cr-V	0.40	1.20	0.08	--	0.30	0.17
5	3 per cent Cr	0.33	3.01	--	--	--	0.12
6	Cr-Si	0.58	8.36	--	--	--	2.50
7	6 per cent Cr	0.18	6.35	--	--	--	1.28

In general, the authors found that, when the stress was high and the temperature was just high enough to cause hydrogen attack, fissuring would then proceed ahead of decarburization. When the temperature was comparatively high and the stress was low, decarburization proceeded ahead of fissuring. Decarburization without fissuring occurred when the steel was subjected to hydrogen under pressure and temperature without applied stress, for instance, in the case of a specimen of steel placed inside a vessel which was maintained at temperature and pressure.

In discussing this paper, Whiteley suggested that the results obtained tended to confirm the hypothesis Williams and Homerberg advanced in 1924 that the liberation of cathodic hydrogen was at the root of the caustic embrittlement of boiler steel. He stated that the type and character of the cracks were very similar in the two cases.

Cox(54), in discussing materials of construction for high-pressure, high-temperature applications, especially those dealing with hydrogen, considered the problems of creep and hydrogen corrosion. He discussed a private communication that told of 168-hour tests at 500 C (930 F) and 3,000 psi in still hydrogen in which Cr-V, Cr-V-Al, Cr-Ni-V-Al, 18-8 stainless, and 24Cr-20Ni steels and BTG metal (12Cr, 60Ni, 2.5W) were completely resistant to hydrogen attack. In service, the 24Cr-20Ni alloy had been exposed to high-pressure hydrogen at temperatures as high as 440 C (825 F) for many thousands of hours without failure. BTG metal was being used regularly at temperatures as high as 565 C (1050 F) under 1000 atm of hydrogen with a fiber stress as high as 25,000 psi, and failures occurred after times of from 2,000 to 20,000 hours; provisions were made so that failure would not result in an accident. Another private communication dealt with the German development of a Cr-Mo-V steel of very low carbon content (approximate composition: 0.06C, 5Cr, 0.75Al, 0.40Mo, 0.05V) for hydrogen-nitrogen service under severe conditions. Another steel, intended for destructive hydrogenation and other reactions with carbonaceous materials, had the composition 0.10C, 6.0Cr, 0.50Mo.

According to Schuyten(59), Sarjant and Middleham conducted numerous tests at 325, 450, and 550 C (615, 840, and 1020 F) and 125 and 250-atm hydrogen pressure for periods of 1,000 to 5,400 hours. Their experiments showed that:

(1) Carbon steel was badly attacked by hydrogen at temperatures as low as 325 C (615 F)

(2) 1.0Cr-V steel showed improved resistance to hydrogen attack

(3) Cr-Al-Mo and Ni-Cr-Mo steels showed even better resistance

(4) 6.0Cr-Mo, 13Cr, 18Cr-8Ni, and 25Cr-20Ni steels were all unaffected by the conditions of exposure.

Naumann(61,62) performed an extensive study of hydrogen attack of steel in connection with the development of materials for the construction of hydrogenation plants to be operated at 450 to 550 C (840 to 1020 F) and 300 to 700-atm pressure. Schuyten(59) has summarized Naumann's work as follows. Naumann studied hydrogen attack on plain-carbon steels, and also investigated the effects of adding various alloying elements. His results showed that plain-carbon steels are attacked severely by high-temperature, high-pressure hydrogen. For example, 100-hour tests showed hydrogen attack starting at 500 C (930 F) at 50-atm pressure, at 400 C (750 F) at 100 atm, and below 350 C (660 F) at 600 atm. Longer exposure times resulted in shifting the resistance limits to even lower temperatures or pressures. Investigation of the effects of alloying elements showed the following:

(1) Silicon, nickel, and copper were not beneficial.

(2) Manganese slightly increased the resistance to hydrogen attack.

(3) Chromium markedly increased the resistance to hydrogen attack, with 3 per cent chromium showing a sudden increased resistance.

(4) Tungsten is better than chromium, and molybdenum is even better than tungsten.

(5) Vanadium, titanium, columbium, tantalum, zirconium, and thorium all give very high resistance to attack above a critical alloy content.

The increased resistance to hydrogen attack conferred by Cr, W, Mo, V, Ti, Cb, Ta, Zr, and Th was attributed to the formation of carbides which are highly resistant to reduction by hydrogen.

Naumann(61,62) found that cold work accelerated the decarburization resulting from hydrogen attack. The decarburization rate was independent of the grain size. He also determined experimentally that a gas containing 90 volume per cent methane and 10 per cent nitrogen was escaping from one of his steels that had suffered severe hydrogen attack.

As part of a study of the action of hydrogen on the constituents of steel, Jacqué(63,64) investigated the reduction by hydrogen of synthetically prepared iron carbide and various chromium carbides. He found that the chromium carbides offered very high resistance to reduction in high-temperature, high-pressure hydrogen.

Schuyten(59) in 1947 pointed out that the trend of development of steels for vessels, fittings, and tubing for high-pressure plants not dealing with high pressures of hydrogen had taken approximately the same course as the development just described of steels intended specifically for exposure to either ammonia-synthesis gas mixture or hydrogen at elevated pressures and temperatures. For general high-pressure service, with the trend to increasing pressures and temperatures, the course was as follows: carbon steel, nickel steel, chromium-nickel and chromium-tungsten steels, chromium-vanadium steel, and finally chromium-molybdenum, chromium-molybdenum-vanadium, and chromium-molybdenum-tungsten steels. The main difference in the two developments was that nickel steels offered no improvement in resistance to hydrogen attack over plain-carbon steels. Resistance to hydrogen attack at elevated temperatures depends on the stability of the carbides present in the steel, and long-time strength at elevated temperatures also depends to a large extent on carbide stability. Most reaction vessels previously had been hollow, forged vessels. However, Schuyten reported on recent developments showing a trend toward welded vessels, particularly of multilayer construction with a high-alloy liner and weep holes through the carbon steel layers or shell to allow escape of hydrogen diffusing through the liner.

Plant experiences derived from hydrocarbon hydrogenation and dehydrogenation processes have been summarized by Schuyten(59). These processes involved hydrogen-to-hydrocarbon molal ratios ranging from 4:1 to 6:1 at pressures of 700 to 900 psi and temperatures from 600 to 925 F.

Examination of equipment showed that coarse-grained, heavy-wall, carbon-steel piping was attacked significantly after periods of 500 to 3,500 hours at 700 to 925 F and pressures from 700 to 900 psi. For example, 40 per cent of the wall thickness was affected after only 500 hours at 860 F. After 14,000 hours of exposure, severe hydrogen attack was found at temperatures as low as 600 F, although no attack at all had been found after 1,200 hours of exposure at that temperature. Similarly, at 860 F, no attack was found after 250 hours, but significant attack was detected after 500 hours' exposure. These results suggest that there is an incubation period before chemical attack occurs. However, during this period of incipient attack, the ductility (as shown by tensile and impact tests) is reduced.

Carbon-molybdenum steel with 0.5 per cent molybdenum showed no hydrogen attack after about 3,000 hours at 700 F and 900-psi pressure, or after 7,000 hours at 750 F and 800 psi. This indicates that the low-cost carbon-molybdenum steels frequently may be suitable for conditions of intermediate severity. No attack was found on either 1Cr-0.5Mo or 2Cr-0.5Mo steels with structures consisting of either ferrite and coarse pearlite or ferrite and very fine pearlite or possibly bainite when exposed at 750 psi and temperatures up to 925 F for periods up to 13,000 hours.

The microstructure of attacked carbon-steel piping from the hydrogenation and dehydrogenation processes was found to consist of three zones:

(1) An inner zone showing complete decarburization and numerous intergranular fissures, generally concentric in nature

(2) A zone of partial decarburization of the channeling type with fissures in the decarburized channels

(3) Unaffected original structure near the outer, unexposed surface.

A carbon-steel laboratory reactor tube that failed in service after 1,100 hours at 900 F and 650-psi pressure was completely decarburized and fissured through 80 per cent of the wall thickness, and the remaining 20 per cent was partially decarburized and contained fissures.

The depth of attack in the hydrogenation and dehydrogenation equipment was found to increase rather sharply with increasing temperature in the range 700 to 925 F and to increase linearly with time once attack had started. Again, the effect of structure was marked; a coarse-grained 6-inch pipe was badly attacked after only 500 hours' exposure at 800 F and 750 psi, whereas fine-grained 1-inch and 1-1/2-inch pipe were unaffected under the same conditions. The adverse effect of welding again was observed, as with exposure to ammonia-synthesis gas mixture, the coarse-grained heat-affected zone adjacent to the weld being more susceptible to attack than the parent metal.

Schuyten(59) prepared the following list of conclusions regarding hydrogen attack of steels, based on considerable plant experience and information from the literature.

(1) Hydrogen attack starts at a limiting temperature and partial pressure of hydrogen as a function of time; the longer the exposure time, the lower

are the minimum temperature and pressure for onset of attack. The higher the temperature, the lower is the limiting pressure, and, conversely, the higher the pressure, the lower is the limiting temperature. Figure 14, which he prepared from information contained in the technical literature, shows limiting curves for attack of carbon steel as a function of temperature and pressure. Curve I is based on 100-hour tests reported by Naumann(61), and Curve II is based on long-time tests of several investigators. The difference between the two curves demonstrates the inadequacy of short-time tests to predict long-time behavior. A similar type of curve could be prepared for each of various alloy steels.

(2) The rate of hydrogen attack increases with increasing temperature and increasing pressure.

(3) Hydrogen attack on steels makes itself manifest by decarburization and intergranular fissuring of the structure. This results in reduced mechanical properties, particularly tensile strength, ductility, and impact strength. Reduction of the carbides also may lead to blisters which form as the result of high pressures developed by the methane reaction product. Under severe conditions, hydrogen also may reduce oxide and sulfide nonmetallic inclusions in the steel.

(4) Once started, hydrogen attack is progressive with increased time. However, frequently an incubation period for the start of chemical attack has been observed.

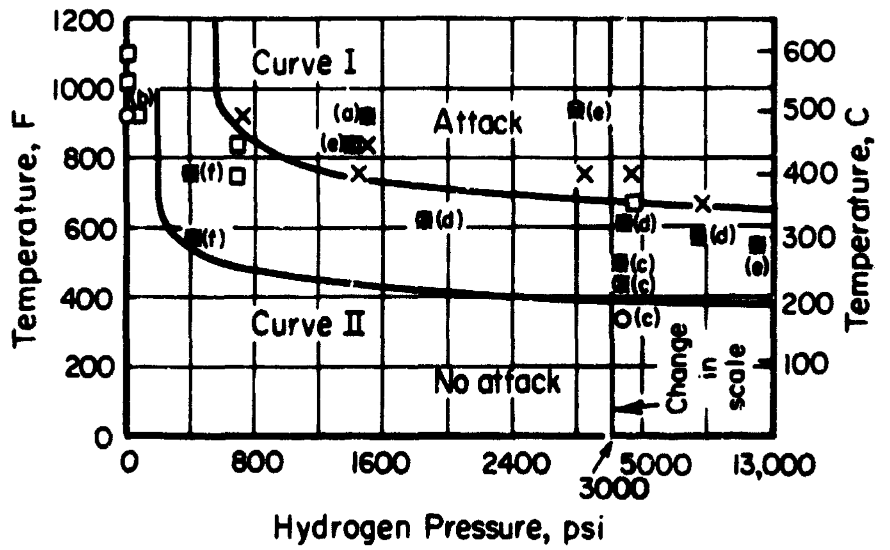
(5) The addition of carbide-forming alloying elements to the steel, such as chromium, molybdenum, tungsten, vanadium, titanium, and columbium, substantially increases the resistance to hydrogen attack, as is shown in Figure 15. Noncarbide-forming elements, such as nickel, copper, and silicon, are not effective in increasing the resistance to attack. Low-alloy steels, such as C-0.5Mo, 1.0Cr-Mo, and 2.0Cr-Mo, show good resistance to hydrogen attack under moderately severe conditions. For conditions of greater severity, 3Cr-Mo and 6Cr-Mo steels and 18Cr-8Ni austenitic stainless steel are used.

(6) Steels with high carbon content are more susceptible to hydrogen attack than are low-carbon steels.

(7) Coarse-grained steels are more susceptible to attack by hydrogen than are steels with a fine-grain structure.

(8) A steel in which the carbide constituent is finely dispersed, such as in the form of very fine pearlite or possibly bainite, has better resistance to hydrogen attack than does a structure consisting of ferrite and coarse pearlite.

A paper by Evans(67) summarized investigations of hydrogen attack on carbon steels in plant equipment. The equipment was handling, at elevated temperatures and pressures, a gas that contained approximately 95 per cent hydrogen, 3 per cent nitrogen, and 2 per cent methane. The pressure averaged 350 psi, and temperatures ranged



Curve I:
Naumann(61)
100-hr tests on 0.11% C steel
× Attack ☐ No attack
Curve II:
(a) Vanick et al.(55)
(b) Cox(54)
(c) Inglis and Andrews(60)
(d) Sarjant and Middleham(65)
(e) Naumann(61)
(f) Zapffe(66)
■ Attack ○ No attack

FIGURE 14. BOUNDARY CONDITIONS FOR HYDROGEN ATTACK ON CARBON STEEL(59)

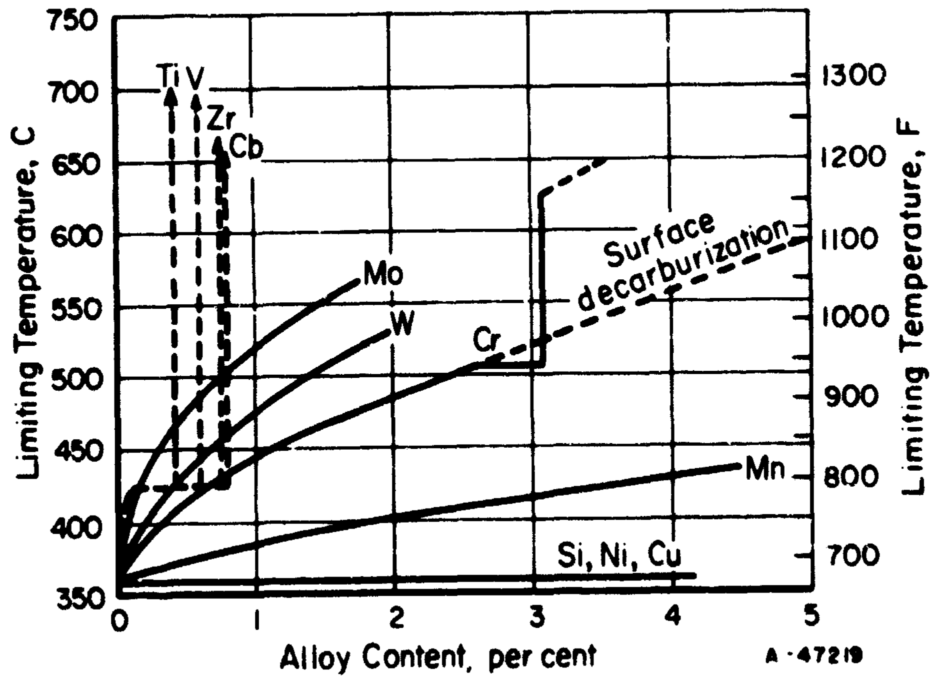


FIGURE 15. EFFECT OF ALLOYING ELEMENTS ON THE RESISTANCE OF STEELS TO ATTACK BY HYDROGEN (AFTER NAUMANN, REFERENCE 62)(59)

0.1% C, 300 kg/cm^2 hydrogen pressure, or 4270 psi, 100 hours.

from 310 to 370 C (590 to 700 F). Seamless tubing, lap-welded pipe, and butt-welded pipe made of low- to medium-carbon plain-carbon steels were used as piping materials. In addition, Toncan iron butt-welded pipe had recently been used to replace portions of the steel pipe. Heat exchangers were made of low-carbon steel plate. Converter shells were made of the same steel as the heat exchangers, but they were lined with AISI Type 430 stainless steel, a material which was found to resist hydrogen attack under the conditions encountered in this system.

The equipment was inspected frequently to guard against failure by hydrogen attack. The results of all of the investigations of the various components are shown in Table 14. The length of time that the sections had been exposed before examination ranged from 6 months to 6 years. Twelve of the investigations disclosed recognizable damage from hydrogen attack. In no case was hydrogen attack found in a component which had been exposed for less than 2 years. However, when found after 2 years' exposure, the attack was in an advanced stage and probably started well before the sampling time. Other sections which had been in contact with hydrogen at equal temperatures and pressures for as long as 4 years showed no signs of attack. All sections that showed attack were made of plain-carbon steels that contained from 0. 10 to 0. 35 per cent carbon. A section of Toncan iron, a low-carbon iron containing small amounts of molybdenum and copper, showed no signs of attack after 20 months' exposure.

Dodge(46) summarized the behavior of 26 different metals exposed to hydrogen for from 4 to 10 weeks at temperatures of 300 to 500 C (570 to 930 F) and pressures of 1,000 and 2,000 atm. The data were obtained with hollow tensile-test specimens subjected to internal hydrogen pressure while being held in furnaces at constant temperature for the desired period of time. Control samples were subjected to the same temperatures but without the hydrogen pressure. At the end of preselected periods of time, the samples were removed from the furnaces and tested to determine the ultimate tensile strength, the elongation, and the reduction in area. For comparison, tests also were made on untreated samples from the same lot of material. Sections of exposed and unexposed specimens were examined metallographically. The following basis was used to evaluate the results: If the specimen exposed to hydrogen had, within reasonable limits of reproducibility, the same tensile properties as the unexposed control sample, it was considered not to have been attacked by hydrogen. If the tensile properties were lowered but the microscope revealed no fissuring, or if heating in the absence of hydrogen essentially restored the properties, the sample was concluded to have been embrittled but not attacked. Finally, if the tensile properties had deteriorated and fissuring was clearly revealed by the microscopic examination, it was concluded that the metal had been attacked.

He summarized his preliminary observations as follows:

(1) Plain-carbon steels, even those of low carbon content, were severely attacked at 400 C (750 F) in a relatively short time. This was to be expected, in view of information contained in the technical literature. At 300 C (570 F), no appreciable attack occurred.

(2) Some alloy steels were attacked severely, others were embrittled, and still others were not affected appreciably. Contrary to expectations, some Cr-Mo steels with as much as 5 per cent chromium were definitely attacked at 2,000 atm, even though the carbon contents were

TABLE 14. SUMMARY OF INVESTIGATIONS OF HYDROGEN ATTACK ON CARBON STEEL AT 350 PSI AND ELEVATED TEMPERATURES IN A MIXTURE OF 95% H_2, 3% N_2, and 2% CH_4(67)

Average Operating Temperature, C	Length of Service	Material	Results of Examination
370	4 years	0.20% carbon-steel pipe	Severe attack
370	4 years	0.14% carbon-steel pipe	Severe attack
365	4 years	Low-carbon steel pipe	No attack
365	2 years	SAE 1035 steel pipe	Severe attack
365	2 years	Low-carbon steel pipe	Indications of attack
365	2 years	0.13% carbon-steel pipe, butt welded	Superficial attack
365	20 months	Low-carbon steel pipe	No attack
365	16 months	SAE 1035 steel pipe	No attack
360	31 months	0.20% carbon-steel pipe, seamless	No attack
360	31 months	0.20% carbon-steel pipe, seamless	No attack
360	31 months	0.20% carbon-steel pipe, seamless	No attack
360	31 months	0.08% carbon-steel pipe, lap welded	No attack
360	31 months	0.08% carbon-steel pipe, lap welded	No attack
360	31 months	0.08% carbon-steel pipe, lap welded	No attack
360	2 years	0.10% carbon-steel pipe, lap welded	Superficial attack
360	20 months	0.06% carbon Toncan iron	No attack
360	6 months	0.06% carbon Toncan iron	No attack
355	6 years	0.20% carbon-steel plate	Heavy attack
355	6 years	0.20% carbon-steel plate	Heavy attack
355	31 months	0.20% carbon-steel pipe, seamless	No attack
355	31 months	0.08% carbon-steel pipe, lap welded	No attack
355	2 years	0.19% carbon-steel pipe, seamless	No attack
355	2 years	0.20% carbon-steel plate	Heavy attack
355	2 years	Low-carbon steel tubing	Indications of attack
320	2 years	Low-carbon steel pipe	No attack
310	4 years	0.10% carbon-steel pipe	Heavy attack
310	2 years	Low-carbon steel pipe	Slight attack
310	20 months	Low-carbon steel pipe	No attack
225	2 years	0.20% carbon-steel pipe	No attack

low (about 0.10 per cent). There was some evidence, though not conclusive proof, of attack on a Cr-Mo steel containing 10 per cent chromium.

(3) High-nickel alloys such as K-Monel, Inconel, and Hastelloy B were either attacked or embrittled.

(4) Some embrittled samples had their original properties restored by heating to somewhat higher temperatures in the absence of hydrogen.

(5) Results on high-chromium alloys, such as Chromax, Nichrome, and Nichrome V, were somewhat inconclusive, in that specimens of Nichrome and Chromax were unaffected while Nichrome V was attacked severely.

(6) It was concluded tentatively that 2,000 atm was a considerably more severe condition than 1,000 atm. Some metals that were not affected appreciably at 1,000 atm were attacked severely or embrittled at 2,000-atm hydrogen pressure.

(7) No effect was observed on any stainless steels, either of the austenitic 300 series or the single steel tested of the 400 series.

Van Ness and Dodge(47) exposed several nickel-base alloys and a number of steels of widely varying composition to hydrogen at 1,000 and 2,000 atm and temperatures up to 500 C (930 F). The materials tested and a qualitative evaluation of the results are shown in Table 15. The authors concluded that the most suitable material for use with high-pressure hydrogen at elevated temperatures probably was austenitic stainless steel. The plain-carbon steel and the four low-alloy steels were not expected to resist hydrogen attack under the high-pressure, high-temperature conditions used. None of these steels had an alloy content sufficient to tie up all the carbon as stable carbides. All of them were severely attacked with the exception of the AISI 4140 samples, which were, however, badly embrittled under the relatively mild conditions to which they were exposed.

In a study of hydrogen attack on more than 50 materials, Perlmutter and Dodge(48) investigated 16 low-alloy steels. Tests were performed in hydrogen at 1,000 and 2,000 atm (15,000 and 30,000 psi) at temperatures up to 500 C (930 F). During the short exposure times used – a matter of days – the influence of temperature was much more pronounced than was that of pressure. Frequently, a difference of 25 C (45 F) was sufficient to bring about a change from complete resistance to hydrogen attack to catastrophic failure, whereas doubling the pressure from 1,000 to 2,000 atm resulted in only a moderate increase in hydrogen attack. The relative importance of temperature changes was discussed further. Whether the mechanisms of attack involved diffusion phenomena or chemical reaction rates, they would be exponential functions of temperature. On the other hand, pressure effects depend on smaller rate-of-change functions, which the authors suggested were probably square roots. Perlmutter and Dodge concluded that their experimental evidence supported these views and indicated that the choice of an alloy for high-temperature, high-pressure service is dependent mainly on the temperature, provided that the mechanical strength of the metal at service temperature is sufficient to hold the pressure.

TABLE 15. QUALITATIVE RESULTS OF EXPOSURE OF SEVERAL STEELS AND NICKEL-BASE ALLOYS TO HIGH-PRESSURE HYDROGEN (1000 AND 2000 ATM) AT TEMPERATURES UP TO 930 F(47)

Material[(a)]	Major Constituents, weight per cent								
	C	Fe	Cr	Ni	Mo	V	W	Ti	Other
High-alloy tool steels					Unaffected				
Nu-die-V steel (q)	0.40	Bal	5.	--	1.35	1.10	--	--	--
Rex AA steel (a)	0.73	Bal	4.	--	--	1.15	18.	--	--
8-N-2 steel (q)	0.79	Bal	4.	--	8.	1.	1.5	--	--
Vasco M-2 steel (q)	0.65	Bal	4.	--	5.	2.	6.	--	--
Type 440C SS (a)	1.04	Bal	17.0	0.26	0.45	--	--	--	--
Ni-base, nonferrous alloys					Embrittled				
K Monel (h)	0.15	--	--	Bal	--	--	--	0.45	Cu = 29, Al = 3
Inconel (r)	0.08	7.5	15.5	Bal	--	--	--	--	--
Inconel X (h)	0.04	7.	15.	Bal	--	--	--	2.5	Cb = 1
Nichrome Alloy V (r)	0.08	--	20.	Bal	--	--	--	--	--
Hastelloy B (r)	0.12	5.	--	Bal	28.	--	--	--	--
High-alloy, Cr-Ni or Ni-Cr iron alloys					Unaffected				
Type 303 SS (a)	0.15	Bal	18.	9.	0.60	--	--	--	--
Type 304L SS (a)	0.025	Bal	18.4	10.6	--	--	--	--	--
Type 310 SS (a)	0.16	Bal	24.9	20.5	--	--	--	--	--
Type 347 SS (a)	0.08	Bal	18.	11.	--	--	--	--	Cb = 10C
Nichrome (r)	0.06	Bal	16.	60.	--	--	--	--	--
Chromax (r)	0.06	Bal	20.	35.	--	--	--	--	--
Low-alloy Ti steels					Embrittled				
Ti steel (a)	0.04	Bal	--	--	--	--	--	0.34	B = 0.02
Ti-Mo steel (a)	0.06	Bal	--	--	0.57	--	--	0.33	--
Cr-Ti-Mo steel (a)	0.05	Bal	2.20	--	0.97	--	--	0.43	B = 0.026
Medium-alloy Cr steels					Embrittled				
5%-Cr steel (q)	0.12	Bal	5.41	--	0.50	--	--	--	--
10%-Cr steel (q)	0.10	Bal	9.57	--	1.10	--	--	--	--
Low-alloy steels[(b)]					Attacked				
Mild steel (r)	0.10	Bal	--	--	--	--	--	--	--
Maxel 3-1/2 steel (q)	0.50	Bal	0.65	--	0.18	--	--	--	--
Halvan steel (q)	0.50	Bal	1.0	--	--	0.20	--	--	--
AISI 4140 steel (q)	0.40	Bal	1.0	--	0.20	--	--	--	--
Double Special (a)	1.30	Bal	--	--	--	--	3.50	--	

(a) a - annealed; h - age hardened; q - quenched and tempered; r - as received.

(b) None of this group of low-alloy steels had an alloy content sufficient to tie up all the carbon as stable carbides. All of them were severely attacked with the exception of the AISI 4140 samples, which were, however, badly embrittled by the relatively mild conditions under which they were exposed.

Under these very high pressures of hydrogen, small additions of chromium and vanadium (up to 1.49 and 0.15 per cent, respectively) did not entirely prevent embrittlement or attack, but appreciably increased the useful life of the material. Armco iron was embrittled by exposure at room temperature to hydrogen at 1,000-atm (15,000 psi) pressure; embrittlement increased progressively with increasing temperature. Since even Armco ingot iron contains a small amount of carbon (about 0.01 per cent), one can conclude that at least the embrittlement is not dependent on large carbon contents in the iron.*

These investigators also tested a group of 11 high-chromium alloys in hydrogen at elevated temperatures and very high pressures. Six were special iron-chromium alloys containing between 10 and 20 per cent chromium; the remaining five were commercial ferritic stainless steels. Most of the straight-chromium ferritic stainless materials were embrittled, but they were resistant to hydrogen attack over the range of conditions tested – up to 2 weeks at 500 C (930 F) under 2,000 atm (30,000 psi) of hydrogen in the severest test. Van Ness and Dodge(47) previously had established the excellent resistance of austenitic stainless steels to high-temperature hydrogen gas. (Austenitic stainless steels also were shown to be resistant to permanent attack by hydrogen-nitrogen mixtures by the work of Maxwell(57), Ihrig(58), and Schuyten(59).)

High chromium content did not confer resistance to embrittlement merely by its presence, nor did increasing the chromium from 10 to 20 per cent in the special alloys or from 11.8 to 27.5 per cent in the commercial stainless steels noticeably alter the resistance to temporary embrittlement. The principal benefit derived from chromium seemed to be protection against decarburization with the attendant loss of strength and the formation of methane which builds up disruptive pressures.

Ciuffreda and Rowland(68) described the hydrogen attack on three carbon-steel fixed-bed catalytic reformer reactors in a petroleum refinery. The carbon-steel reactors failed by high-temperature hydrogen attack at a location of high stress, the first failure occurring approximately 1 year after startup. The three reactors operated in series on a naptha-hydrogen vapor-phase mixture at approximately 925 F and a hydrogen partial pressure of 330 psi. The shells, fabricated from silicon-killed carbon steel (ASTM A201, Grade B), were internally insulated in an attempt to maintain the shell temperature at approximately 300 F. This temperature was chosen as being well below that at which hydrogen attack would be predicted, based on Nelson's curves for hydrogen attack(69) (to be discussed later). However, within 1 month after startup, it was found that the shell temperatures over large portions of the reactors averaged between 600 and 750 F, temperatures far higher than had been anticipated. The high shell temperatures were attributed primarily to hot hydrogen-rich reactor vapors contacting the inner surface of the steel shell. It was decided to continue operations and to order shrouds for installation to reduce shell temperatures. Extensive shell-temperature data were obtained, and maximum allowable shell operating temperatures and pressures were established based on allowable stresses. Limits were not based on consideration of hydrogen attack, because it was believed that such attack would not be serious before the shrouds could be installed. The first failure occurred approximately 1 year from startup. An extensive investigation was carried out to determine the extent of the damage and the feasibility of repairing the reactor shells.

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*In the section on kinetics to be presented later in this report, it will be shown that a "high-purity" iron that contained only [illegible] ppm ([illegible] per cent) carbon was attacked by hydrogen at elevated temperatures. However, the mechanism of attack for that material was different from that of SAE 1020 steel or a high-purity Fe-[illegible] per cent C alloy.

It was learned that hydrogen attack had occurred on A201 steel in 1 year with a hydrogen partial pressure of 330 psi wherever the metal temperature had been above 575 F. Actual failure occurred where the metal temperature had averaged 740 F. Hydrogen attack had been more severe as the steel temperature increased above 575 F, just as would be expected. It was found that stress affected the location of the failure in steel attacked by hydrogen. With sufficiently high stress, failure occurred in areas which were not the most severely attacked by hydrogen. Also, it was observed that a "transition" period existed for hydrogen attack during which the steel suffered permanent loss in ductility but showed no positive evidence of this in the microstructure. In the most severely attacked areas, decarburization took place completely through the 1-5/8-inch-thick shell wall, and fissuring occurred to a maximum depth of approximately 3/4 inch.

SPECIAL STUDIES RELATED TO HYDROGEN ATTACK OF STEEL AT ELEVATED TEMPERATURES AND PRESSURES

Irreversible Hydrogen Attack

Allen et al.(70) studied the time for irreversible, or permanent, hydrogen attack on steel in the temperature range from 700 to 1000 F and at hydrogen pressures ranging from 400 to 1,400 psi. Test materials were a high-purity vacuum-melted iron, a high-purity vacuum-melted carbon steel, and a commercial SAE 1020 steel. Solid test specimens were exposed to the high-temperature, high-pressure hydrogen in autoclaves and, therefore, were not subjected to internal pressure or tensile stresses. The hydrogen gas used had a minimum hydrogen content of 99.9 per cent and contained less than 20 ppm of oxygen; it had a specified dew point of -75 C (-103 F). Gas samples taken from the autoclaves after exposure of the specimens indicated a dewpoint below -50 C (-58 F). After damage was produced by exposure to hydrogen, the specimens were vacuum degassed at elevated temperatures to remove absorbed hydrogen. This served to remove temporary, or reversible, embrittlement so that only the permanent, or irreversible, embrittlement would be detected in a tensile test. The mechanical properties and results of structural examinations revealed the extent of permanent damage.

The effects of exposure to hydrogen at 700 F and 1,400 psi on the stress-strain curves of SAE 1020 steel are shown in Figure 16. Note the disappearance of the yield point with sufficient exposure. The ultimate tensile strength of all test materials was reduced by exposure to hydrogen at the elevated temperatures and pressures. The loss in ductility resulting from hydrogen attack (as measured by reduction in area in a tensile test) was primarily related to the relative orientation of the textural arrangement of the fissures with respect to the direction of principal stresses. The microscopic fissures that developed during attack subdivided the specimen into many small segments of short length. Although the bridges of material between the fissures fractured in a ductile manner in the tensile test, the fissures limited the amount of plastic flow and the overall elongation and reduction in area, as would be expected. Thus, the loss in ductility was caused primarily by the geometric structure and not by an inherent embrittlement of the steel itself.

The effect of test temperature on the exposure time for 50 per cent permanent hydrogen attack* of SAE 1020 steel is shown in Figure 17 for the annealed condition and for different amounts of cold reduction. Figure 18 shows the effect of hydrogen pressure on the exposure time to cause 50 per cent hydrogen attack. Also, the rate of attack was quite dependent on hydrogen pressure. The vacuum-melted high-purity 0.2 per cent carbon steel was attacked faster than was the commercial SAE 1020 steel.

In the annealed SAE 1020 steel, the fissures developed along what might have been the former austenite grain boundaries. The majority of fissures developed selectively at the interface between ferrite grains and pearlite colonies, not along the ferrite-cementite interface of the pearlite. Ultimately, the fissures progressed along ferrite grain boundaries. During this process, the cementite of the pearlite was gradually diminishing and simultaneously spheroidizing. Progressive recrystallization and grain growth of the ferrite occurred simultaneously with decarburization. With increasing prior cold work, the fissures became more aligned in the rolling direction. Hydrogen attack of high-purity iron occurred by the formation of many very small fissures along grain boundaries.

These investigators also found that cold work prior to exposure to hydrogen at 900 psi and temperatures between 700 and 1000 F significantly reduced the time to achieve 50 per cent attack on SAE 1020 steel. Figure 19 shows that 39 per cent cold reduction in area reduced the time for 50 per cent attack to as little as 10 per cent of the time for the vacuum-annealed steel. Small degrees of cold work became more significant at the higher temperatures (see 1000 F curve). They also found that cold-worked steel which was recrystallizing while exposed to the high-temperature, high-pressure hydrogen was damaged faster and to a greater extent than was steel which had been recrystallized before exposure. Whereas the annealed steel and that cold reduced 5 per cent exhibited an incubation time for attack, the properties of the steel cold reduced 39 per cent in area decreased immediately upon exposure to hydrogen. Figure 20 shows the effect of exposure time and of cold work on the true fracture stress for SAE 1020 steel. The effects of exposure on the ultimate tensile strength and the strain to fracture of SAE 1020 steel cold reduced 5 per cent in thickness prior to exposure is shown by the stress-strain curves in Figure 21. Similar data for material cold reduced 39 per cent are shown in Figure 22. During the exposure, two reactions occurred that had opposing effects on ductility; hydrogen attack tended to reduce ductility, and the recovery and recrystallization tended to increase ductility. The net effects are shown in Figures 21 and 22.

In discussing this paper by Allen, et al., Backenstro reported on studies which indicated that a trace of water is required to catalyze hydrogen attack at elevated temperatures. In experiments in which the hydrogen contained between 15 and 35 ppm of water, surface decarburization and a permanent loss of ductility were obtained in carbon steel after 7 days at a temperature of 500 F and a pressure of 500 psi. Decarburization increased with time and temperature. The decarburization rate was very slow at temperatures below 750 F and very rapid at temperatures higher than 1000 F. These results could not be duplicated when hydrogen containing essentially no water was used. When water-saturated hydrogen was used, the decarburization rates were more rapid than the rates obtained with hydrogen that contained 15 to 35 ppm of water.

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*All the data which were obtained in this investigation were plotted in diagrams showing the property (ultimate tensile strength, yield strength, elongation, true fracture stress, critical bending angle in a bend test, hardness, and specific gravity) as a function of exposure time in hydrogen. The time at which 50 per cent of the property change occurred was determined from these diagrams. Observation of the different properties showed only small differences in the time for 50 per cent attack. In order to indicate the effect of temperature on the rate of attack, the exposure time necessary to cause 50 per cent attack was plotted on a logarithmic scale versus the inverse absolute temperature.

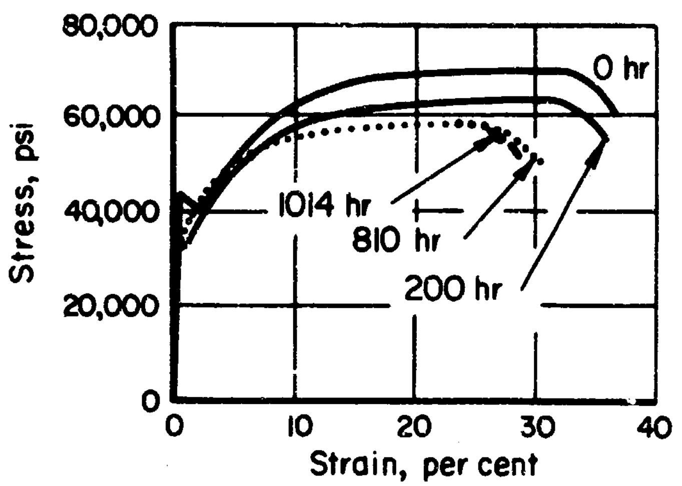

FIGURE 16. STRESS-STRAIN CURVES OF ANNEALED SAE 1020 STEEL FOR VARIOUS TIMES OF EXPOSURE TO HYDROGEN AT 1,400-PSI PRESSURE AND 700 F TEST TEMPERATURE(70)

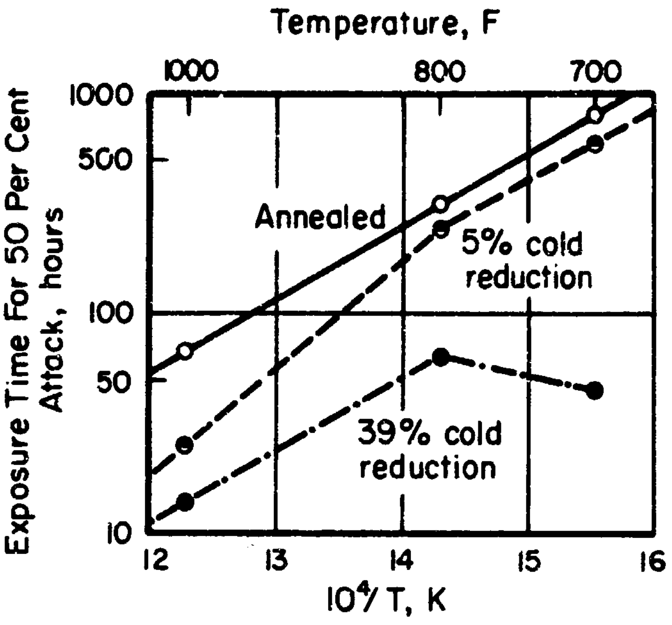

FIGURE 17. EXPOSURE TIME FOR 50 PER CENT HYDROGEN ATTACK, AS A FUNCTION OF THE TEST TEMPERATURE FOR SAE 1020 STEEL(70)

See the footnote on page 43 for an explanation of the exposure time for 50 per cent attack.

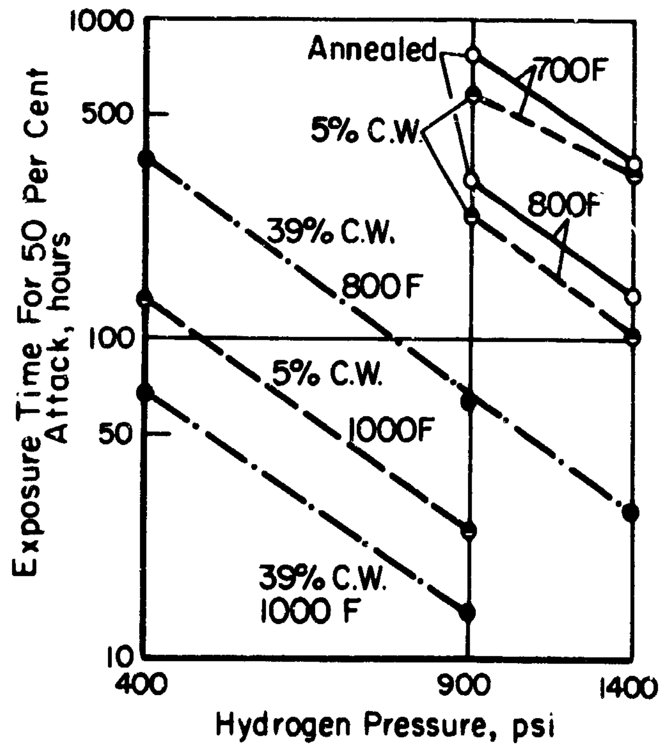

FIGURE 18. EFFECT OF HYDROGEN PRESSURE ON THE TIME REQUIRED TO CAUSE 50 PER CENT HYDROGEN ATTACK IN SAE 1020 STEEL(70)

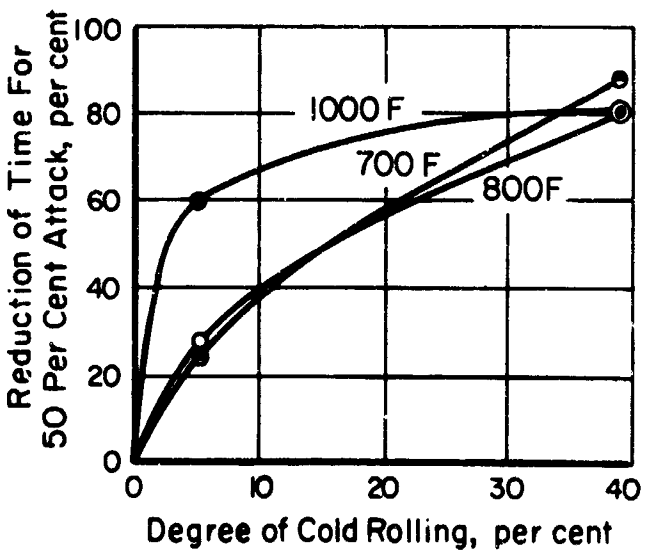

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FIGURE 19. EFFECT OF COLD WORK ON THE TIME REQUIRED TO CAUSE 50 PER CENT HYDROGEN ATTACK OF SAE 1020 STEEL AT 900-PSI HYDROGEN PRESSURE(70)

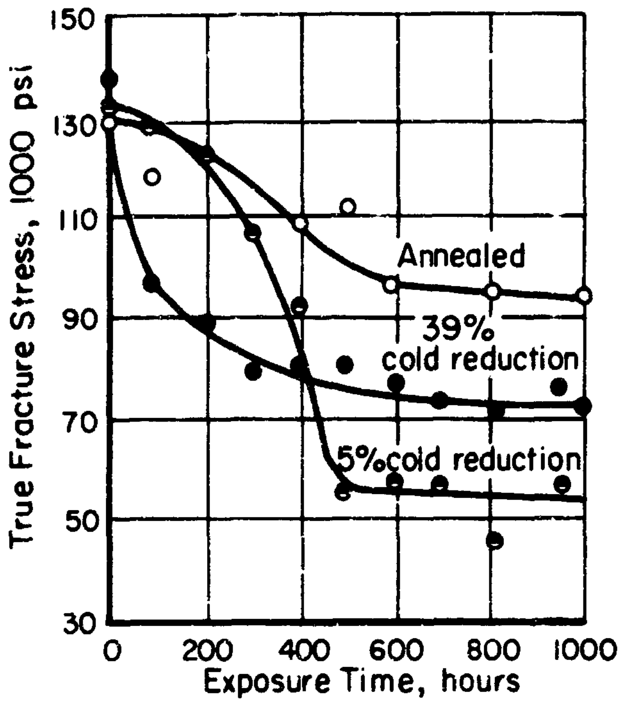


FIGURE 20. STRESS AT FRACTURE OF SAE 1020 STEEL IN DIFFERENT INITIAL CONDITIONS AS A FUNCTION OF TIME OF EXPOSURE TO HYDROGEN AT 1,400-PSI PRESSURE AND 700 F TEST TEMPERATURE(70)

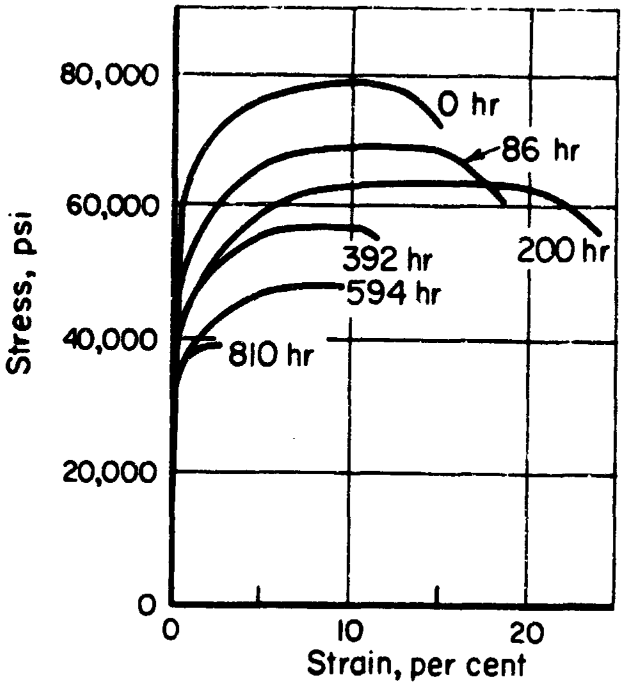


FIGURE 21. STRESS-STRAIN CURVES OF 5 PER CENT COLD-ROLLED SAE 1020 STEEL FOR VARIOUS TIMES OF EXPOSURE TO HYDROGEN AT 1,400-PSI PRESSURE AND 700 F TEST TEMPERATURE(70)

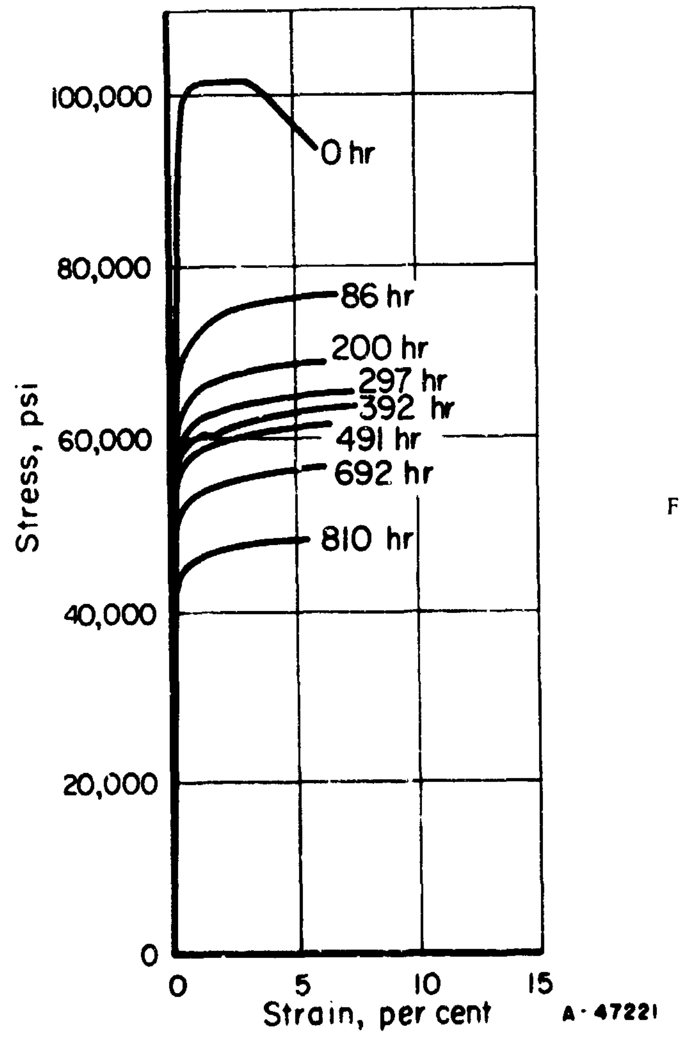


FIGURE 22. STRESS-STRAIN CURVES OF 39 PER CENT COLD-ROLLED SAE 1020 STEEL FOR VARIOUS TIMES OF EXPOSURE TO HYDROGEN AT 1,400-PSI PRESSURE AND 700 F TEST TEMPERATURE(70)

Creep

Most of the work on hydrogen attack of steel at elevated temperatures that has been discussed in this report has been concerned with the effect of exposure at elevated temperatures on the properties measured at room temperature. However, structural components usually are subjected to stress while exposed to hydrogen. Not only may stress have an effect on the kinetics of the attack, but hydrogen may alter the creep properties of the steel. The effect of hydrogen environments on the creep-rupture properties of steels has been the subject of a limited number of investigations, for example see References 71 and 72. However, these studies were carried out at such low hydrogen pressures that hydrogen attack did not occur to any appreciable extent. Kolgatin and co-workers(73) used tubular specimens stressed by internal pressure of hydrogen under conditions where hydrogen attack could occur. A commercial iron and various alloy steels were studied, and all showed a great decrease of endurance (long-time strength) in hydrogen as compared to tests in a nitrogen atmosphere. In hydrogen, the failures were of the brittle, intercrystalline type, but the failures of specimens exposed to nitrogen were accompanied by appreciable deformation.

Chernykh and co-workers(74) also studied the influence of hydrogen on the long-time strength of steels. They, too, used hollow specimens stressed by internal pressure. They found that the long-time strength of all three steels tested was lower when the stress was created by hydrogen pressure than when nitrogen was used, and this difference increased with an increase in the time required for rupture. Also see Reference 75 for a continuation of this work.

In the tests described above, hydrogen pressure was not held constant. Therefore, Allen, Rosenthal, and Vitovec(76) undertook an investigation in which a tensile load was applied to the specimens, so as to more accurately determine the role of stress in the behavior of steel under conditions of hydrogen attack. This work was performed with normalized SAE 1020 steel at 800 and 1000 F in environments of argon at 50 psi and hydrogen at 400-, 900-, and 1,400-psi pressure. The fracture stresses for the tests in hydrogen were lower than those obtained in argon, even at the shortest fracture times investigated. Under conditions of exposure severe enough to produce fissuring, the stress-rupture curve consisted of three straight-line segments, as illustrated in Figure 23. In the short-time segment (high tensile stresses), the fracture stresses obtained in hydrogen were 12 to 40 per cent lower than those obtained in argon. This segment of the curve was little influenced by variations in hydrogen pressure. The second segment of the curve had a much greater slope, and the loss of strength as compared to argon increased to 60 per cent. Because this part of the curve was associated with hydrogen attack of the carbides in the steel, presumably by the methane reaction, it was sensitive to pressure. The specimens that fractured during the time interval represented by the third portion of the curve were completely decarburized prior to rupture. In this stage, the rupture stress decreased only slightly with increasing time to fracture. A comparison with prior work on unstressed specimens showed that the rate of hydrogen attack was accelerated by creep. Ductility, which also was decreased by the hydrogen environment, was sensitive to hydrogen pressure over the entire range of fracture times.

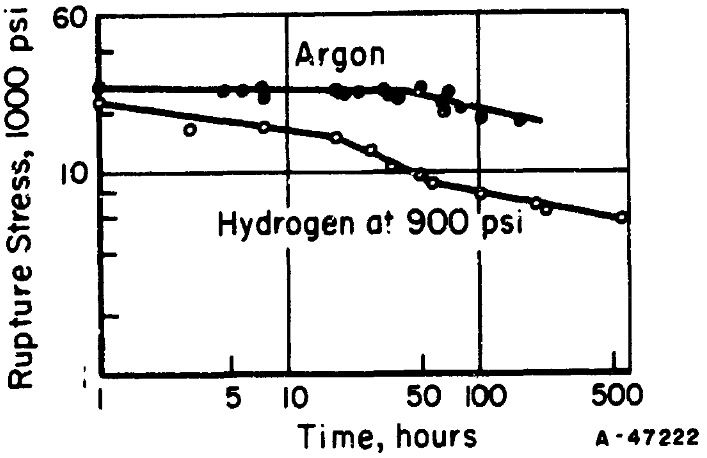


FIGURE 23. STRESS-RUPTURE CURVES FOR SAE 1020 STEEL AT 1000 F IN ARGON ATMOSPHERE AND IN HYDROGEN ATMOSPHERE AT 900-PSI PRESSURE(76)

A program to determine the effect on several materials of a special gas which contained 5 per cent H_2 and 95 per cent N_2 and which was about 70 per cent saturated with water vapor was described by Baughman(77). The gas was essentially at atmospheric pressure in these experiments, but it was flowing at a rate of 5 cu ft/hr through the small furnace capsule that surrounded the specimen. One phase of the program was to establish the influence of the special gas environment on the elevated-temperature rupture properties of six widely used high-temperature alloys. Sufficient data were accumulated on each alloy to provide design data for assemblies including both sheet and bar fabrication incorporating welded and/or brazed construction. Tests were made on parent metal, welded joints, brazed joints, and notched specimens. Similar specimens were tested in air for comparison. The alloys were A-286, L-605, X-40, R-41, Inco 702, and U-500; thus, they included iron-base, nickel-base, and cobalt-base materials. The rupture strength of these alloys was markedly reduced when stressed in the gas environment as compared to their strength in air. The strength of Inco 702 was reduced by 50 per cent; this alloy was the most severely impaired by the gas environment. The average reduction was about 15 to 20 per cent. The strength of the brazed and welded materials was affected more than was the strength of the parent metal for the four materials tested in these conditions.

Class(78) discussed the creep resistance and the creep-rupture strength of steels resistant to hydrogen under pressure. The effects of hydrogen and test temperature for a German steel of the 21 CrVMoW 12 type used for tubes and accessories up to about 520 C (970 F) in hydrogen atmospheres are shown by the following data:

Steel Composition, per cent	
C	0.18-0.25
Mn	0.30-0.50
Si	0.15-0.35
Cr	2.7 -3.0
Mo	0.35-0.45
V	0.75-0.85
W	0.30-0.45

Time for Steel Tubes to Rupture Under 700-Atm Pressure of Hydrogen or Nitrogen

Test Temperature			
C	F	Test Gas	Rupture Time, hr
600	1112	Nitrogen	~8,000
600	1112	Hydrogen	$\leq$100
545	1013	Hydrogen	~8,000

Kinetics

Most investigators seem to believe that hydrogen attack at elevated temperatures and pressures is due to the chemical reaction between hydrogen and carbides (internal decarburization) at the grain boundaries of the steel, resulting in methane whose pressure builds up, causing localized grain-boundary fissuring and thus giving rise to additional deterioration of the material. (This will be discussed in the next section of this report.) However, Weiner(79) contends that this model fails to explain satisfactorily many observations of this phenomenon. Therefore, he undertook a fundamental investigation of irreversible hydrogen embrittlement, the permanent embrittlement resulting from decarburization and manifested as intergranular fractures accompanied by reduced ductility and strength, also commonly called hydrogen attack. This work was still in progress when a short paper was published on the kinetics of hydrogen attack(79).

The data were obtained with a low-carbon killed steel subjected to a hydrogen pressure of 700 psi. A series of specimens was exposed for various times at each of four selected temperatures (800, 900, 1000, and 1100 F). Subsequent to exposure, the specimens were baked at 400 F in a nitrogen atmosphere to remove residual hydrogen and thus eliminate any cause of reversible hydrogen embrittlement. Then tensile tests were performed at room temperature. In this work, hydrogen attack was defined as the per cent loss in reduction of area on small, round tensile specimens.

Figure 24 shows plots of per cent hydrogen attack as a function of the exposure time, t_E. Each point on the curves represents the mean value of results from three or four specimens. The curves all have the same shape. Each can be considered to be made up of four segments: (1) an incubation time, t_o, prior to which no permanent damage occurs (as detected by the criterion selected), (2) a high rate of attack occurring over a short time interval (2 to 4 hours) in which the material proceeds to an advanced stage of embrittlement, (3) a decreasing transient rate, and (4) a low, steady-state rate of attack. Whether this same kinetic pattern applies to all materials and all types of exposure still remains to be determined.

From Figure 24, it is evident that up to 1000 F the effect of exposure time, t_E, on the kinetics of hydrogen attack was primarily manifested as a pronounced effect on the incubation time, t_o. However, the data for exposure at 1100 F suggest that above about 1000 F, another process has become important. The new process acts in a direction opposite to that of the rate-controlling process operative at temperatures of 1000 F and below. No definite effects of exposure temperature, T_E, on the rate of attack were observed.

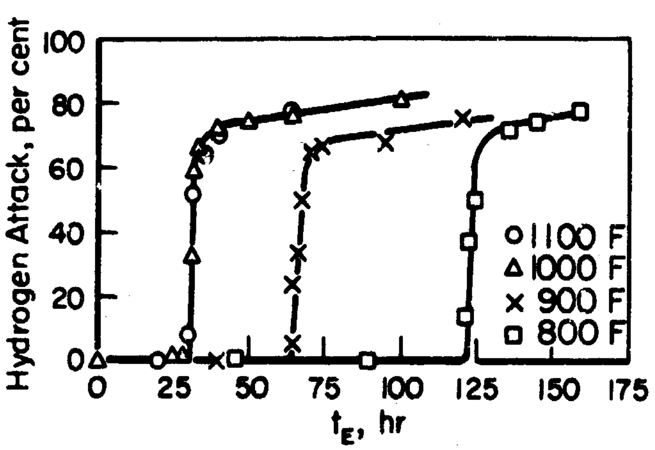


FIGURE 24. HYDROGEN ATTACK VERSUS EXPOSURE TIME AT 700-PSI HYDROGEN PRESSURE FOR A LOW-CARBON KILLED STEEL[(79)]

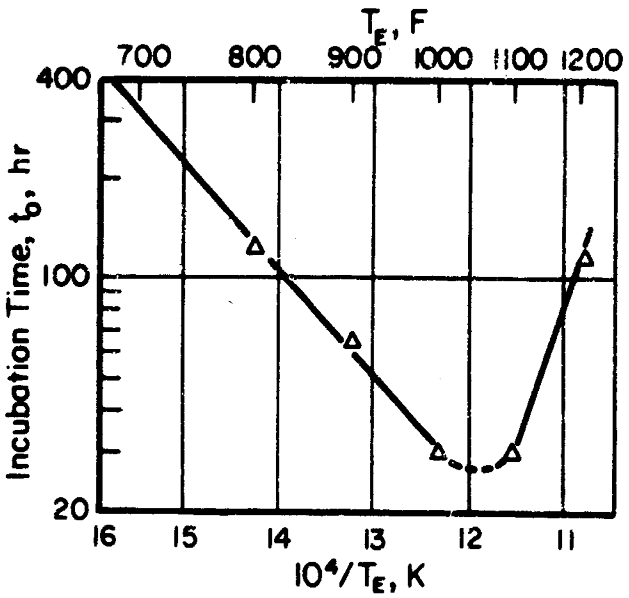


FIGURE 25. INCUBATION TIME AS A FUNCTION OF TEMPERATURE FOR HYDROGEN ATTACK ON A LOW-CARBON KILLED STEEL AT 700-PSI PRESSURE(79)

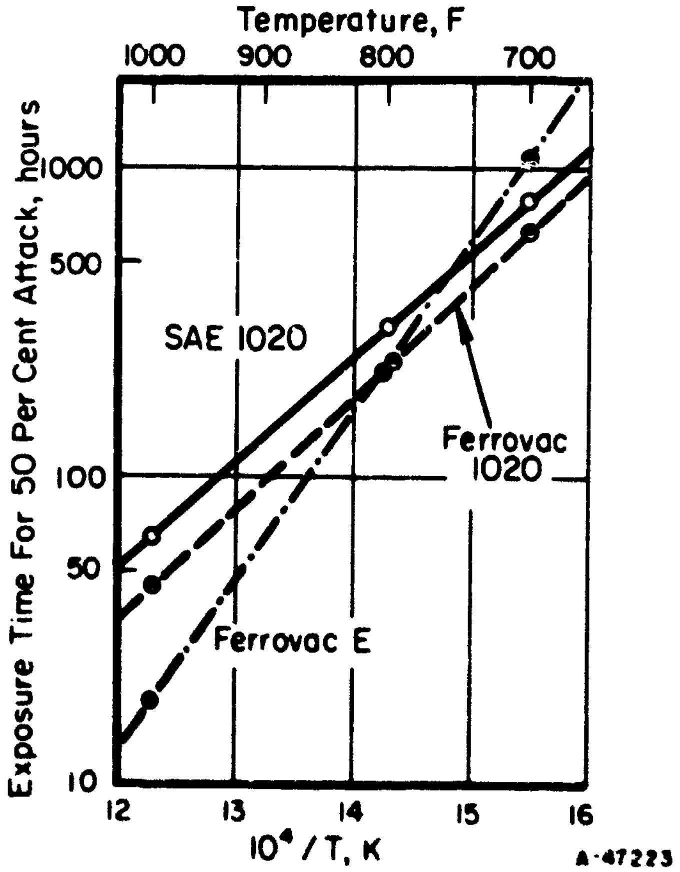


FIGURE 26. EXPOSURE TIME FOR HYDROGEN ATTACK AS A FUNCTION OF THE TEST TEMPERATURE FOR SAE 1020 STEEL, FERROVAC 1020 STEEL, AND FERROVAC E IRON(70)

All the data which were procured in this investigation were plotted in diagrams showing the property as a function of exposure time in hydrogen. The time at which 50 per cent of the property change occurred was determined from these diagrams. Observation of different properties showed only small differences in times for 50 per cent attack. In order to indicate the effect of temperature on the rate of attack, the exposure time necessary to cause 50 per cent attack was plotted on a logarithmic scale versus the inverse absolute temperature.

A plot of ln t_o versus $1/T_E$ (T_E in degrees Kelvin) resulted in the C-curve shown in Figure 25. Up to 1000 F a straight-line relationship was observed which could be represented by the following equation:

$$t_o = A e^{(Q/R T_E)} = 3.78 \times 10^{-3} e^{(14,600/R T_E)} \text{ for } P_{H_2} = 700 \text{ psi} ,$$

where T_E is exposure temperature in degrees Kelvin, and A, Q, and R are constants, the latter being the gas constant. The authors concluded that the value of 14,600 cal/mole obtained for Q rules out the simple diffusion of carbon or hydrogen in iron acting as the rate-controlling process in hydrogen attack at temperatures up to 1000 F (based on data by Wert and by Stross and Tomkins, respectively).

Allen, Jansen, Rosenthal, and Vitovec(70) also studied the rate of irreversible hydrogen attack of steel at elevated temperatures. They exposed high-purity iron, SAE 1020 steel, and a high-purity Fe-0.20C alloy to hydrogen at 1400 psi and temperatures of 700, 800, and 1000 F. Their data suggest an activation energy of 15,200 cal/mole for hydrogen attack of SAE 1020 and Ferrovac 1020 steel. They found that, at the high test temperature, the high-purity iron was attacked more rapidly than were the carbon steels, whereas at 700 F the iron was attacked more slowly than the steels (see Figure 26). Also, an activation energy of 25,200 cal/mole was obtained for the high-purity iron (Ferrovac E). Thus, their findings indicate that the mechanism of attack of the relatively pure iron is different from that in the carbon steels.

GENERAL CONSIDERATIONS OF HYDROGEN ATTACK

The phenomenon of chemical attack of steel by hydrogen gas has been the subject of several investigations. The principal ones were

	Max Temp,		Max Pressure,
	F	C	atm
Campbell, 1919(27)	1920	1050	1
Cox, 1933(a)(54)	1050	565	1000
Inglis and Andrews, 1933(60)	930	500	250
Sarjant and Middleham, 1937(65)	1020	550	250
Jacqué, 1936(80)	1020	550	145
Naumann, 1937, 1938(61,62)	1110	600	970
Schuyten, 1947(a)(59)	925	495	900
Nelson, 1949, 1951(a)(81,69)	1110	600	700
Van Ness and Dodge, 1955(47)	930	500	2000
Perlmutter and Dodge, 1956(48)	930	500	2000
Ciuffreda and Rowland, 1957(68)	820	440	22
Allen, Jansen, Rosenthal, and Vitovec, 1961(70)	1000	540	95
Allen, Rosenthal, and Vitovec, 1962(76)	1000	540	95

(a) Primarily review papers with some plant data reported. For these investigators, the maxima refer to the plant data.

Also, much work has been done on the effects of hydrogen-rich ammonia-synthesis gas mixture on steels, some of the more important investigations being as follows:

	Max Temp, F	Max Temp, C	Max Pressure, atm
Wheeler, 1922(a)(51)	1380	750	1
Vanick, 1923 to 1927(52,53,55)	930	500	100
Kosting, 1934(56)	570	300	600
Maxwell, 1936(57)	930	500	1000
Schuyten, 1947(b)(59)	885	475	130
Ihrig, 1949(58)	1100	595	1000

(a) These data are Wheeler's own experimental results. He also reported some plant results at 500 C and 100 atm.

(b) Primarily a review paper with some plant data reported. For this investigation, the maxima refer to the plant data.

The following general conclusions regarding high-temperature, high-pressure hydrogen attack of carbon steel were drawn from a study of the literature by Ciuffreda and Rowland in 1957(68).

(1) Under certain conditions of temperature and hydrogen partial pressure, atomic hydrogen permeates and decarburizes steel by reducing iron carbide (Fe_3C) to form methane (CH_4). The pressure of the methane, which cannot diffuse from the steel, may exceed the cohesive strength of the steel and cause intergranular fissuring. With fissuring, a significant permanent loss in ductility of the steel results.

(2) The severity of hydrogen attack increases with increasing temperature and increasing hydrogen partial pressure.

(3) Usually, attack occurs in three stages: 1, diffusion of atomic hydrogen into the steel; 2, decarburization; and 3, intergranular fissuring.

(4) A steel which has undergone only the first stage of hydrogen attack suffers a loss in ductility which is considered to be temporary because ductility can be restored by a relatively low-temperature heat treatment. Permanent, irreversible embrittlement results when the attack has progressed to the second and third stages. The term "hydrogen attack", as used in this report, refers to this second- or third-stage attack which causes permanent damage, and not to first-stage, or temporary, attack.

(5) There has been no systematic study made of the effect of time on the temperature-pressure limits for the start of attack.

Because the attack of steel by hydrogen is associated with decarburization and internal fissures, the external appearance after exposure cannot be correlated with the extent of attack, nor does any thinning of the section take place.

The reaction of hydrogen with iron carbide to form methane is believed to be the important chemical reaction in the hydrogen attack of steels. For example, see References 61,58,67,59,46,82,68,70 and 83. Naumann(61,62) experimentally determined that a gas containing 90 volume per cent methane (CH_4) and 10 per cent nitrogen was escaping from one of his steels that had suffered severe hydrogen attack.

Hydrogen reacts with graphite and cementite according to the equations:

$$C + 2\,H_2 = CH_4$$

$$Fe_3C + 2\,H_2 = 3\,Fe + CH_4\,.$$

Since both of the above reactions are exothermic, methane in contact with iron is stable at comparatively low temperatures. The rate of the reactions in the direction from left to right in the above equations is very small at low temperatures. However, increased pressure favors decarburization, since a contraction occurs when 2 molecules of hydrogen react to produce 1 molecule of methane. In iron-carbon alloys, cementite (Fe_3C) is more susceptible to attack by hydrogen than is graphite.

This reaction of hydrogen and iron carbide is believed to occur at grain boundaries throughout the steel, and not just at the surface. Therefore, since methane is unable to diffuse out of the steel, very high localized gas pressures are developed which ultimately cause fissures to form. Many investigators have shown that steel definitely is decarburized and that fissures are developed by hydrogen attack at elevated temperatures and pressures. This accounts for much of the damage to steel. Even if no methane were to form, decarburization alone would lower the tensile strength considerably. Fissures, however they may be formed, would be expected to drastically lower the ductility and the strength of the steel.

The reaction with carbon is not the only one possible. Severe attack has occurred with some low-carbon alloys, and it is possible that other reactions with hydrogen, such as the reduction of oxide or sulfide inclusions or hydride formation, are important. Some of these reactions could produce gases other than methane that would not diffuse through steel and therefore could build up high localized pressures, too. Also, any reaction which reduced the volume of the solid could form voids, and these could serve as sites for the precipitation of molecular hydrogen and the build up of high pressures with their disruptive effect, since molecular hydrogen does not diffuse through steel. However, it has been observed that steels of high carbon content generally are more susceptible to hydrogen attack than are those of low carbon content.

Decarburization of steel by high-pressure hydrogen takes place at elevated temperatures, about 500 F or higher. The decarburization appears to be nil at room temperature, as might be expected. The pressure appears to be a less important variable in the hydrogen attack of steel than is the temperature. The main effect of increased hydrogen partial pressure seems to be to speed up the attack or to cause it to take place at somewhat lower temperatures.

As has been shown previously in this report in discussions of the work of various investigators, the reaction of hydrogen with the carbides in steel can be prevented or minimized by adding various carbide-stabilizing elements to the steel. These include such elements as chromium, tungsten, molybdenum, vanadium, titanium, and columbium, and, to a lesser extent, manganese. Titanium and vanadium are particularly effective in quite small amounts.

The effectiveness of carbide-stabilizing elements in steel has been evaluated by a survey covering many types of steels and a wide variety of commercial processes using hydrogen at high temperatures and pressures. From the data obtained, it was possible to define what were considered to be safe operating limits for carbon and various low-alloy steels in hydrogen service. These limits were shown in a figure originally prepared by Nelson in 1951(69) and presented with accompanying references. According to Nelson and Effinger writing in 1955(82), these data had been used as a basis for the design of many high-pressure, high-temperature hydrogen processes and in no instance where the required alloy content was adhered to had hydrogen damage been reported.

Information obtained over a period of several years showed the proposed limits to be adequate and in certain installations to be slightly on the conservative side. However, about 1958, new information was obtained concerning failures of carbon steel at low pressures and very high temperatures. They indicated that, in long-time service, welded carbon steel suffers hydrogen attack under conditions less severe than those which would be resisted by steel in the unwelded condition. Therefore, Nelson(84) added a curve on his chart to indicate safe operating limits for carbon steel fabricated by welding. Also, a slight adjustment was made to the limit for unwelded carbon steel, incorporating data on long-time performance. The revised chart is shown in Figure 27. The curves for the low-alloy steels remained the same as on the 1951 chart.

It is seen from Nelson's chart that only austenitic stainless steels are satisfactory at all temperatures and pressures encompassed by the chart (see the note regarding austenitic stainless steels in the legend). From the data in the figure, it would appear that plain-carbon steels are suitable for operating temperatures up to 450 F at a hydrogen pressure of 2000 psi, up to 525 F at 500 psi, and up to about 960 F at pressures of 120 psi or less. No hydrogen attack would be expected at lower temperatures than those given. Apparent permissible service temperatures for steels in hydrogen at any pressure (up to about 14,000 psi) are as follows:

Type of Steel	Apparent Permissible Temperature, F
Plain-carbon steel	430
0.5Mo	620
1.0Cr-0.5Mo	620
2.0Cr-0.5Mo	750
3.0Cr-0.5Mo	1000
6.0Cr-0.5Mo	1125

The effect of pressure seems to level out at about 3,000 psi. However, not many data are available for pressures higher than this. As mentioned previously, failures have been reported at room temperature for pressures of 2,000 atm (29,000 psi)(45) and for an alloy steel at 3,000 atm (44.000 psi)(46).

Nelson and Effinger(82) pointed out that the Cr-Mo steel of lowest alloy content shown on the 1951 chart is 1.0Cr-0.5Mo. In the late 1940's, a 0.5Cr-0.5Mo steel was developed for resistance to graphitization in high-temperature applications. It was expected by them that this type of steel would find a useful application for hydrogen service as well. Although no operating data were available to them, they believed that the limit for this steel would be midway between the limit for the 0.5Mo and the 1.0Cr-0.5Mo steels.

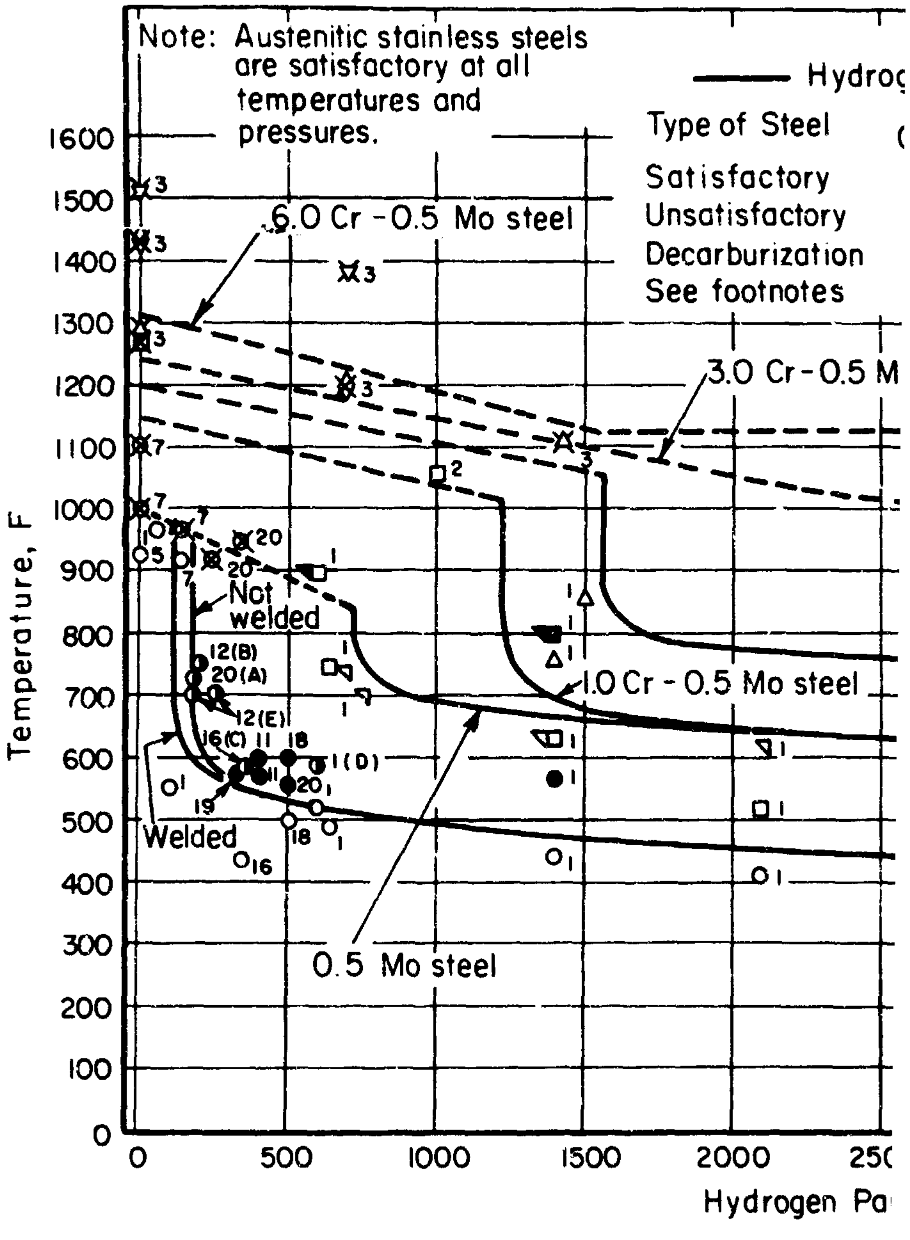
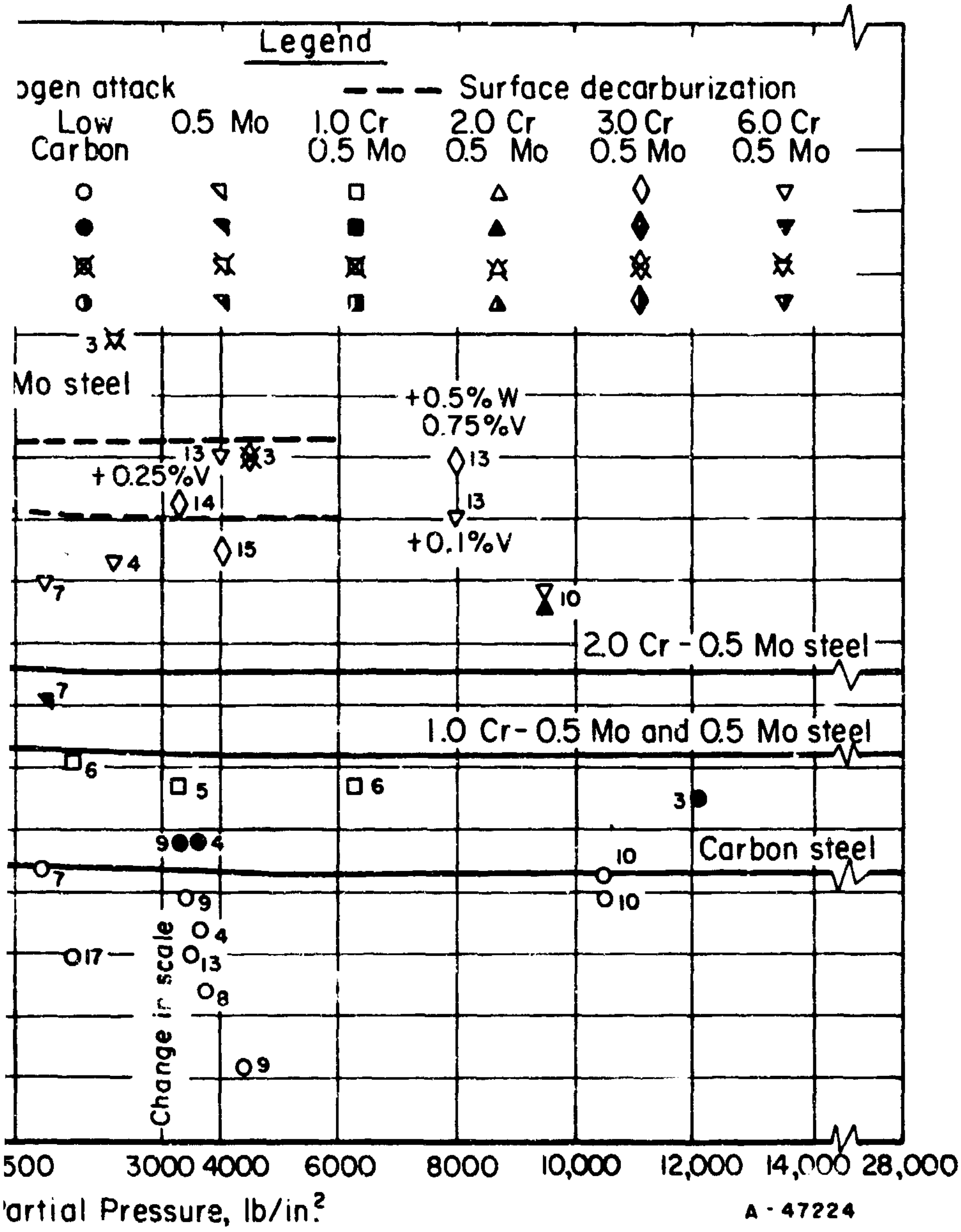


FIGURE 27. OPERATING LIMITS FOR CARBON AND ALLOY STEELS IN



IN CONTACT WITH HYDROGEN AT HIGH TEMPERATURES AND PRESSURES(84)

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*Private communications.

FOOTNO

(A) A section made of A106 pipe was found to be attacked to 27% of its thickness after 57

(B) The attack was concentrated in the overheated section of a hot-bent steel elbow. Th

(C) In a series of 29 steel samples, 12 were attacked while the other 17 were not.

(D) After two years' exposure, 5 out of 6 pieces of carbon steel pipe were attacked. One

(E) Attack was concentrated in the weld and heat-affected sections of A106 pipe. Metal

FIGURE 27. (C

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London, 1936.

29, 1956, pp 103-107.
Sec. III – Refining, 22nd Mid-Year Meeting, May 15,

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745 hours. Other pieces of pipe in the same line were unaffected.
he straight portions of the elbow which had not been heated were not affected.

e piece of pipe was unaffected.
l on each side of this zone was unaffected.

ONTINUED)

Nelson's curves are not applicable to the problem of hydrogen embrittlement, but show only resistance to hydrogen attack (permanent damage).

Class(78) has given considerable information on a number of German steels that are resistant to hydrogen under pressure and that contain between 2 and 3 per cent chromium. These are the preferred steels for high-pressure construction in Germany.

Little is known regarding the ductility of steels while in service at high temperatures exposed to high-pressure hydrogen. Apparently no serious brittle failures have been reported in steels which are resistant to decarburization and fissure formation that result from hydrogen attack. However, Nelson and Effinger(82) pointed out that in addition to the permanent damage to steels by high-pressure, high-temperature hydrogen, operators of hydrogenation plants are aware of a temporary but slight embrittling effect of hydrogen while the plant is in operation. They concluded that this slight embrittling effect is apparently of little consequence unless the part has been subjected to high stresses at sharp notches, such as the roots of threads. Failures of this type have caused breakage of certain highly stressed interior bolts. This has been observed when equipment has been opened for inspection, and it is usually not possible to establish the time of failure, whether it occurred during operation or while cooling down as the plant was being shut down. However, properly designed shells and pressure vessels have performed satisfactorily under conditions of exposure where appreciable hydrogen was diffusing through the steel. According to Nelson and Effinger(82), when hydrogenation plant equipment operating at temperatures in the vicinity of 1000 F in which the steel is known to contain absorbed hydrogen has been cooled from the operating temperature at a rate of 50 to 75 F per hour, no breakages have resulted. It would appear that this rate of cooling is low enough to allow most of the absorbed hydrogen to effuse from the steel without leaving excessive loss of ductility. The precaution also should be taken of designing the piping in hydrogen plants to hold expansion stresses to a minimum.

These steels used in the construction of hydrogenation equipment still retain considerable ductility while hydrogen is present in the steel. Although they become somewhat less ductile when charged with hydrogen than they are prior to exposure, they certainly are not brittle when the term is used to mean no measurable plastic deformation at failure. In spite of a temporary decrease in ductility, there remains sufficient ductility in the steel for many processes to operate normally. Nelson and Effinger(82) have illustrated the degree by which ductility is reduced by comparing the room-temperature elongation of steels before and after exposure to high-pressure, high-temperature hydrogen; this comparison is shown in Table 16. The material exposed to hydrogen was in the form of premachined test bars.

TABLE 16. ROOM-TEMPERATURE TENSILE ELONGATION BEFORE AND AFTER EXPOSURE TO HYDROGEN AT TEMPERATURES UP TO 1000 F AND AT A PRESSURE OF 3500 PSI(82)

Type of Steel	Duration of Test, hours	Elongation in 2 Inches, per cent	
		Before	After
Plain carbon	4,000	42	7
DM (1.3Cr-0.5Mo)	26,000	36	26
3.0Cr	4,000	25	14
5.0Cr	4,000	31	26
5.0Cr	14,000	3[illegible]	10
18Cr-8Ni	4,000	65	44
18Cr-8Ni	14,000	65	39

PREVENTING HYDROGEN ATTACK

Four types of measures have been offered to prevent or limit attack of steel by hydrogen at elevated temperatures and pressures. These include: (1) alloying steel with carbide stabilizers, (2) monobloc construction of resistant nonferrous alloys, (3) use of liners of resistant alloys, and (4) use of nonoccluder coatings.

As shown in Figure 27, plain-carbon steels are entirely satisfactory for exposure to hydrogen in processes that are carried out at fairly low temperatures and relatively high pressures, or at low pressure and relatively high temperatures. At high temperatures and high pressures, however, increasing amounts of suitable alloying elements are required to provide resistance to the decarburizing action of hydrogen on steel. The effects of the various alloying elements have been discussed previously, so they will only be summarized here. Silicon, nickel, and copper are not effective in increasing the resistance of a steel to hydrogen attack. The reason for this behavior is that these elements do not form stable carbides but go into solution in the ferrite. Manganese additions result in slightly increased resistance, because manganese forms the carbide Mn_3C; however, this carbide is not very resistant to hydrogen. On the other hand, chromium additions substantially increase the resistance to hydrogen attack because the various complex iron-chromium carbides formed are especially resistant to attack. Also, some of the chromium dissolves in the ferrite and reportedly decreases hydrogen diffusibility. Even greater resistance to hydrogen attack is provided by additions of molybdenum or tungsten to the chromium-containing steel. These, also, are believed to stabilize the iron carbide. The elements titanium, vanadium, columbium, tantalum, zirconium, and thorium form stable carbides that are not appreciably soluble in cementite (Fe_3C) and which are highly resistant to attack by hydrogen. Because they are not very soluble in iron carbide, these last-named elements do not provide much of an increase in the resistance to hydrogen until they are present in sufficient quantity to tie up all the carbon in the steel. The elements of this type most often used are titanium, vanadium, and columbium. The amounts theoretically required are as follows: for titanium, four times the carbon content is required to correspond to the formula TiC; a vanadium-to-carbon ratio of 5.7 to 1 corresponds to V_4C_3; and a columbium addition at least eight times the carbon content is required to tie up all the carbon as CbC. . In practice, the minimum contents of these alloy additions would be somewhat greater than the stoichiometric quantities. However, these elements do not provide corrosion resistance to hydrogen sulfide at elevated temperatures, and they present difficulties in forging. Therefore, frequently these alloy additions are used in lesser amounts in combination with chromium and molybdenum. Figure 15 shows the effects of the various alloying elements on the resistance of steels to hydrogen attack.

Chromium-molybdenum steels are widely used for equipment in contact with hydrogen at elevated temperatures and pressures. For conditions just beyond the capabilities of carbon steels, a 1.0Cr-0.5Mo steel may be suitable. As the operating conditions become more severe, the chromium content is increased, as indicated in Figure 27. For many processes, steels containing 2-3 per cent chromium and 0.5-1.0 per cent molybdenum have been widely used. In more recent years, steels of the Cr-Mo-V and Cr-Mo-V-W types have seen some service. The Germans developed the N-10 hydrogenation alloy steel with the following nominal composition: 0.18-0.25C, 0.30-0.50Mn, 0.15-0.35Si, 2.7-3.0Cr, 0.35-0.45Mo, 0.75-0.85V, and 0.30-0.45W. After a special normalizing and tempering treatment, this steel is reported to show a very high resistance to hydrogen attack, although it apparently is not immune to slow attack after long exposures at 560 C (1040 F) and 700-atm pressure of hydrogen.

For the most severe conditions of service, particularly if resistance to hydrogen sulfide is required in addition to resistance to hydrogen attack, austenitic stainless steels, often the 18Cr-8Ni type, are used.

In some high-pressure, high-temperature processes, heavy-walled vessels and piping of solid alloy steel are used. As indicated above, this can be entirely satisfactory provided the alloy content is high enough to resist the decarburizing effect of the hydrogen under the intended service conditions. However, alloy-steel vessels of large sizes can be quite expensive, and there are limits to the wall thickness that can be supplied in alloy steel. To overcome these problems, plain-carbon steel vessels with special alloy liners often are used. The internal liner eliminates direct contact of high-pressure hydrogen with the nonresistant steel. The material to be used for the liner should be resistant to hydrogen attack under the conditions to be encountered in the intended application. As indicated in the work of Perlmutter and Dodge(48), several nonferrous metals and alloys meet this requirement. Liners of alloy steel with sufficient alloy content also will resist attack, and these often are used because of cost and availability considerations. Austenitic stainless steels find wide use, because they are suitable for the most severe applications and are readily available.

Liners of alloy and stainless steels do not prevent the diffusion of hydrogen, not even under the conditions in which they are resistant to attack. Thus, hydrogen will diffuse through these liners and will accumulate between the liner and the plain-carbon steel shell. Even though hydrogen diffuses through the liner, so long as the liner material is resistant to decarburization, cracking, and blistering, it is merely necessary to provide protection for the shell against the hydrogen that could accumulate between it and the liner. This usually is done by machining continuous spiral grooves on the inside of the shell or the outside surface of the liner, or by providing many tiny weep holes drilled through the shell. This venting of the hydrogen to the atmosphere prevents the pressure buildup that could attack the load-bearing shell.

According to Nelson and Effinger(82), considerable experience has proved that the areas of contact where a liner is welded to a carbon-steel shell, such as in strip lining or intermittent spot welding, are not sufficient to cause damaging amounts of hydrogen to enter the carbon steel. Multiwall or layer-built vessels are easily adapted to this technique; the inner sheet is alloy steel and subsequent layers are constructed of carbon steel.

Another method is to use a solidly bonded inner liner of alloy sufficient to resist the hydrogen, which is applied to an appropriate steel backing. The liner is used only when it is necessary to resist corrosives such as hydrogen sulfide. Frequently the liner is austenitic stainless steel. In this construction, the hydrogen diffusing through the liner would attack the backing material. Therefore, the backing steel must be of such an alloy composition that it will resist the effect of hydrogen which will diffuse through the liner.

Hydrogen attack of steel depends not only on pressure, but on the temperature of the steel. For all but the very highest pressures, attack can be avoided by lowering the temperature sufficiently. Some pressure vessels have been constructed in which the vessel wall is used as a heat-transfer surface, thereby lowering the temperature of all except perhaps the inner surface layer of the metal to a safe value. This type of design usually permits use of carbon or low-alloy steel in place of a more costly steel of higher alloy content. In exothermic hydrogen processes, this arrangement also provides a means of temperature control and possible recovery of heat.

Nelson and Effinger(82) have pointed out other design and operating considerations for process equipment used in high-pressure, high-temperature hydrogen reactions. Hydrogen-charged steels suffer a loss in ductility when cooled to ambient temperatures, as has been discussed earlier in this report. Apparently, there are no data to show whether a similar loss in ductility occurs at operating temperatures. Therefore, it is considered good practice in the design of equipment for hydrogen service to avoid stress raisers. Since they might become points of high stress concentration, sharp recesses, threaded connections, and rough welds are to be avoided. Welding should be of superior quality with no slag inclusions or blowholes present, as these could allow hydrogen or reaction products to accumulate and build up pressures that promote cracking of the weld. It is imperative that the alloy content of the deposited weld metal be at least as high as the alloy content of the plate.

Rapid temperature fluctuations should be avoided. At high temperatures, the steel can contain considerable hydrogen, because the solubility for hydrogen is relatively high and diffusion is rapid. If the steel is cooled quickly, the hydrogen becomes trapped in the metal and, because the metal is supersaturated with atomic hydrogen, molecular hydrogen tends to accumulate at voids, inclusions, and other discontinuities. High pressures can build up which produce high stresses in the metal; these stresses may become high enough to cause blisters or cracks to form. Also, since the metal becomes less ductile with a higher hydrogen content, expansion and contraction stresses may cause further permanent damage to the steel. Therefore, maximum cooling rates have been specified for some hydrogen-processing equipment to limit contraction strains so that they do not become excessive. A maximum cooling rate of 75 F per hour is specified for some equipment.

Many nonferrous alloys resist hydrogen attack, but for solid, monobloc construction of large equipment, their cost usually is prohibitive or their low strength makes their use impracticable. Where safety considerations are the overriding factor, the best choice of material usually is austenitic stainless steel or deoxidized beryllium copper(83,48). Hydrogen diffuses through both of these materials. However, it does not produce reactions which build up disruptive pressures of gaseous reaction products, it does not promote delayed, brittle failure under static loading, and it seldom affects the ductility seriously. Their use has been recommended in situations where a brittle failure would constitute a serious safety hazard(83). However, recent work has shown that even austenitic stainless steel can be appreciably embrittled when very large hydrogen contents (in the order of 50 cc/100 grams of steel) are present*(85).

Tardif and Marquis(83) have discussed the possibilities of using coatings to mitigate hydrogen attack. Coatings of certain metals, particularly, zinc, cadmium, aluminum, and tin (also beryllium, magnesium, tellurium, lead, antimony, and bismuth) have been proposed to stop hydrogen diffusion. These are nonoccluders which are semipermeable to hydrogen. Since information on the hydrogen permeability in these metals is meager, such proposed use is only tentative. When tried, these coatings generally have been unsuccessful, due to hydrogen diffusion through the coatings at the higher temperatures, porosity of the coatings, or to mechanical difficulties.

The results of a recent investigation(86) indicate that two metals – tungsten and gold – are completely impermeable to hydrogen. A process is being developed to chemically deposit gold on steel, and preliminary results indicate that steel can be protected

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* Tensile strength reduced to 80 per cent of initial value and reduction in area reduced from a value of 80 per cent to 55 per cent.

from hydrogen by a thin coating of gold. Apparently no suitable technique is available to deposit tungsten on steel so as to exclude hydrogen from the steel.

With all of these possible metallic coatings, application by electroplating generally should be avoided because of the codeposition of hydrogen which produces embrittlement of the steel being coated. Chemical deposition has limited application; many of the metals are less noble than iron, and even with the elements that are below iron in the electromotive series, the reaction often is extremely slow. Vapor deposition seems to offer more promise. Cadmium has been applied to steel by this method without the embrittlement that usually is encountered with electroplating. However, it has been shown that the cadmium does not prevent the introduction of hydrogen into the steel by subsequent corrosive or electrochemical attack of the coated part.

Apparently, no information is available on the resistance of nonmetallic materials, such as organic paints or plastics, to permeation by hydrogen.

The results of limited studies have shown that oxide films retard the penetration by hydrogen. This effect can be appreciable in certain alloys of high chromium and aluminum contents. Huffine and Williams(87) found that the steady-state permeation rate through an oxidized Fe-Cr-Al alloy was some three orders of magnitude lower than that through the clean metal at the same elevated temperature. However, in cases in which the oxide film is reducible by hydrogen, the permeation rate increases as the reaction removes the film, and approaches the value obtained for the clean metal. Much work remains to be done in the development of surface coatings that would be impermeable to hydrogen.

Internal insulation may be used to keep vessel walls at a low temperature, thereby reducing susceptibility to hydrogen attack and improving creep strength.

DETECTION OF HYDROGEN ATTACK

Frequently, it is necessary to check equipment for hydrogen attack. Since hydrogen attack involves no loss of metal, there is no reduction in metal thickness. Actually, the thickness tends to increase slightly. Often, the surface exposed to the hydrogen-bearing atmosphere gives no visible indication that attack has occurred, though sometimes blisters or cracks are visible. Often the cracks are so small they are visible only under a microscope. Therefore, the usual methods of detecting corrosion in the field, that is, visual examination and direct measurement, are not applicable.

The most reliable methods of detection involve destructive tests. The usual procedure is to remove core or ring sections from the equipment for testing. Since the decarburization resulting from hydrogen attack lowers the hardness of the steel substantially, hardness tests performed on the exposed surface or on a cross section will qualitatively indicate the existence and depth of decarburization. The presence of fissures also will reduce the hardness value obtained.

Another simple test and one which can be performed in the field is a bend or flattening test. An embrittled sample will break at a much lower bend angle than steel of normal ductility. For severe embrittlement, the sample may break before assuming any permanent bend. When such field-detection methods indicate that hydrogen attack has occurred, they should be supplemented by laboratory investigations.

Laboratory studies commonly include hot-acid macroetching (1:1 HCl, 160-175 F, perhaps 30 minutes) to reveal fissures and cracks, metallographic examination to determine the extent of decarburization and detect the presence of fissures, 180-degree reverse-bend tests to detect the loss of ductility, and tensile tests for a more complete examination for the loss in mechanical properties (tensile strength, elongation, and reduction in area). Even a very small sample will permit chemical analysis for carbon content to determine how much the carbon has been depleted from its original level. Ultrasonic inspection also is useful in detecting the presence of microscopic cracks. Evans(67) used a combination of 180-degree reversed-bend tests to detect loss of ductility, macroetching in hot acid to display fissuring, and metallographic examination of a polished-and-etched sample to show the presence of decarburization and fissuring. In a tensile test of material that has merely been embrittled by hydrogen, only the elongation and reduction in area are changed. Chemical attack lowers the tensile strength, changes the shape of the stress-strain curve, and generally is accompanied by severe loss in ductility. Although the impact test of notched specimens is not suitable for revealing hydrogen embrittlement, which is a low-strain rate process, the impact test finds considerable use in detecting permanent damage resulting from hydrogen attack. To more clearly distinguish between the temporary embrittlement and the permanent damage incurred as the result of hydrogen attack, metallographic examination and recovery heat treatments may be used.

The practice of removing samples from equipment in contact with high-pressure, high-temperature hydrogen after various periods of operation has often been recommended. By examining these samples, one can determine whether hydrogen attack has occurred and whether the attack has been progressive.

BOILER EMBRITTLEMENT

At least as early as 1924, it was suggested that liberation of cathodic hydrogen and its penetration into the steel was the cause of boiler embrittlement and caustic cracking of steel.(88) Several investigators since have favored this possibility, and others have raised arguments against it. Even today, opinion is divided as to whether the hydrogen attack is important under service conditions in boilers(89). Smialowski in his recent book <u>Hydrogen in Steel</u>(35) states his opinion that these arguments against hydrogen playing such a role are not absolutely convincing in the light of recent knowledge of the action of hydrogen on steel. He believes that, at high temperatures, hydrogen is liberated from water according to the following reactions:

$$3\,Fe + 4\,H_2O \rightarrow Fe_3O_4 + 4\,H_2 \qquad \text{(below 570 C or 1060 F)}$$

$$Fe + H_2O \rightarrow FeO + H_2 \qquad \text{(at higher temperatures)} \ .$$

Also, as shown by Mohr in 1930, hydrogen sulfide probably is formed in boilers as a product of reduction of sulfates by hydrogen:

$$Na_2SO_4 + 4\,H_2 \rightarrow Na_2S + 4\,H_2O$$

$$Na_2S + 2\,H_2O \rightarrow H_2S + 2\,NaOH \ .$$

Thus, he concludes that in high-pressure boilers, all conditions favoring hydrogen penetration into the steel are present; this includes a partial pressure of hydrogen, hydrogen sulfide, high pressure, and high temperature. Smialowski pointed out that Schroeder observed that certain additions to hot sodium hydroxide, including Sb_2O_3, accelerated the stress-corrosion cracking of steel. Since antimony acts as a poison for the hydrogen recombination into the molecular state, permitting atomic hydrogen more opportunity to enter steel, he feels the part played by hydrogen in the embrittlement of boilers is obvious. Smialowski gives no further discussion of these complicated phenomena in his book, but he concludes that further work is indispensable in this important field of investigation.

CONCLUSIONS

Under certain conditions, hydrogen is able to permeate solid steel. Gaseous molecular hydrogen does not readily permeate steel at ambient temperatures, not even at pressures up to several thousand psi. At high temperatures and pressures, molecular hydrogen is partially dissociated into the atomic form, the degree of dissociation increasing as the temperature increases. This thermally dissociated, or atomic, hydrogen can enter the steel and can cause either temporary or permanent damage. The damage to steel is only temporary so long as the hydrogen is driven out of the steel by a suitable thermal treatment before decarburization, blistering, or cracking begins. This temporary condition usually is referred to as hydrogen embrittlement. However, once decarburization, intergranular cracking, or blistering has occurred, the damage is permanent. The steel loses tensile strength by decarburization and cracking, and it becomes permanently embrittled as the result of crack formation. The processes resulting in permanent damage generally are called hydrogen attack.

There are two important aspects to the problem of steel exposed to hydrogen at high temperatures and pressures. One is a purely physical action involving penetration of hydrogen into the crystal lattice with consequent disruptive effects, and the other is a chemical reaction between hydrogen and various elements present in small amounts in the steel, primarily carbon. The former effect also can occur at ambient temperatures in the case of atomic hydrogen liberated by electrochemical action or by corrosive attack. However, decarburization does not occur at the lower temperatures.

At 1-atm pressure, gaseous molecular hydrogen can be heated to moderately elevated temperatures in a steel container without the steel undergoing permanent damage. However, decarburization occurs at higher temperatures. Even small amounts of hydrogen in the atmosphere of an annealing furnace may cause embrittlement of steel. An increase in pressure reduces the temperature at which rapid attack begins. Moist hydrogen is more effective in decarburizing steel than is dry hydrogen. Steels containing appreciable amounts of strong carbide-forming elements offer improved resistance to decarburization by high-temperature hydrogen.

At ordinary temperatures, hydrogen gas can be handled safely in carbon-steel equipment at pressures up to several thousand psi, but as the pressure is increased above about 30,000 psi dangerous embrittlement can occur. Once steel is penetrated by hydrogen at ordinary temperatures and extreme pressures, thereafter it is permeable at much lower pressure. Austenitic stainless steel and beryllium copper are especially resistant to hydrogen under these conditions. When chromium or aluminum form a stable oxide film on the surface of steel, the resistance to high-pressure hydrogen at room temperature is improved.

At high temperatures and pressures, hydrogen or gas mixtures containing appreciable hydrogen can be especially destructive to many steels. The steel can be seriously weakened by decarburization and by the formation of many microscopic fissures without external evidence of the damage. The problem is commonly encountered in the synthetic-ammonia process and a number of hydrogenation and dehydrogenation processes. The synthetic-ammonia process involves 3:1 hydrogen:nitrogen mixtures that contain a few per cent ammonia at pressures which may be in the range of 1500 to 2000 psi and temperatures up to about 885 F. Under these conditions, coarse-grained carbon steels with a structure consisting of ferrite and pearlite are attacked slightly at temperatures as low as 390 F after exposure for a few years but the attack generally is severe at temperatures above 570 F. However, certain Cr-Mo steels are resistant to hydrogen attack even at 885 F. For the alloy steels, a very fine pearlitic structure produced by normalizing and tempering is considerably more resistant to hydrogen attack than is coarser pearlite. Also, fine-grained structures are more resistant than are coarse-grained ones. Grain coarsening in the heat-affected zone of a weld may cause an otherwise resistant material to be susceptible to hydrogen attack.

Factors that determine the degree of attack are temperature, pressure, stress, exposure time, composition of the steel, and structure of the steel. Hydrogen attack of steel starts at a limiting temperature and partial pressure of hydrogen as a function of time; the longer the exposure time, the lower are the minimum temperature and pressure for onset of attack. The higher the temperature, the lower is the limiting pressure, and conversely, the higher the pressure, the lower is the limiting temperature. Hydrogen attack on steels is manifest by decarburization, intergranular fissuring, and sometimes blistering. This results in reduced tensile strength, ductility, and impact strength. The rate of hydrogen attack increases with increasing temperature and pressure. Attack is an exponential function of temperature, whereas the rate-of-change functions are much smaller for pressure effects. Therefore, temperature is relatively more important than pressure in selecting a steel for high-temperature, high-pressure hydrogen service. Once started, the hydrogen attack is progressive with increased time. However, an incubation period often precedes the start of chemical attack. Cold working accelerates the decarburization resulting from hydrogen attack.

The addition to the steel of carbide-forming alloying elements, such as chromium, molybdenum, tungsten, vanadium, titanium, and columbium, substantially increases the resistance to hydrogen attack. This effect is attributed to the formation of carbides that are highly resistant to reduction by hydrogen. Noncarbide-forming elements, such as nickel, copper, and silicon, are not effective in increasing the resistance to attack. Additions of chromium, tungsten, or molybdenum to steel progressively improve the resistance to hydrogen attack. Additions of vanadium, titanium, columbium, tantalum, zirconium, and thorium all give very high resistance to attack when present in amounts greater than a critical value. Certain low-alloy steels, such as C-0.5Mo, 1.0Cr-Mo, and 2.0Cr-Mo, show good resistance to hydrogen attack under moderately severe conditions. For more severe conditions, 3Cr-Mo, 6Cr-Mo, and 18Cr-8Ni austenitic stainless steel are used. Austenitic stainless steel is especially resistant to permanent damage. High-carbon steels are more susceptible to hydrogen attack than are low-carbon steels. Coarse-grained steels are more susceptible than fine-grained ones. Also, a steel in which the carbide constituent is finely dispersed, such as in the form of very fine pearlite, has better resistance to hydrogen attack than does one that contains coarse pearlite.

The loss in ductility that accompanies the irreversible, permanent, hydrogen attack of steel is caused primarily by the development of fissures, and not by an inherent embrittlement of the steel itself. Also, cold work prior to exposure to hydrogen at elevated temperatures and pressures significantly reduces the time for initiation of permanent attack.

The creep-rupture strengths of steels are lower when stressed in hydrogen at elevated temperatures than when stressed in argon, air, or nitrogen. The rate of hydrogen attack is accelerated by creep.

Studies of the kinetics of irreversible hydrogen attack of steel indicate that the process is different at temperatures above about 1000 F than it is at lower temperatures. Also, the mechanism of attack of relatively pure iron is different from that of carbon steels.

The reaction of hydrogen with iron carbide to form methane is probably the most important reaction in the hydrogen attack of steel. This decarburization of steel by high-pressure hydrogen takes place at elevated temperatures – about 500 F or higher. Because the attack of steel by hydrogen is associated with decarburization and internal fissures, the external appearance after exposure cannot be correlated with the extent of attack. The most reliable methods of detection involve destructive mechanical tests (such as bend, impact, and tensile tests), metallographic examination, and carbon analyses of samples removed from the equipment that has been in contact with high-temperature, high-pressure hydrogen.

Measures used to prevent or limit attack of steel by hydrogen at elevated temperatures and pressures include alloying steel with carbide stabilizers, use of liners of resistant alloy steels, and use of resistant nonferrous alloys. Attempts are being made to develop nonoccluder coatings.

Some investigators are of the opinion that boiler embrittlement and the caustic cracking of steel are caused by atomic hydrogen.

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