

SPECIAL REPORT

on

REVIEW OF LITERATURE ON HYDROGEN
EMBRITTLEMENT

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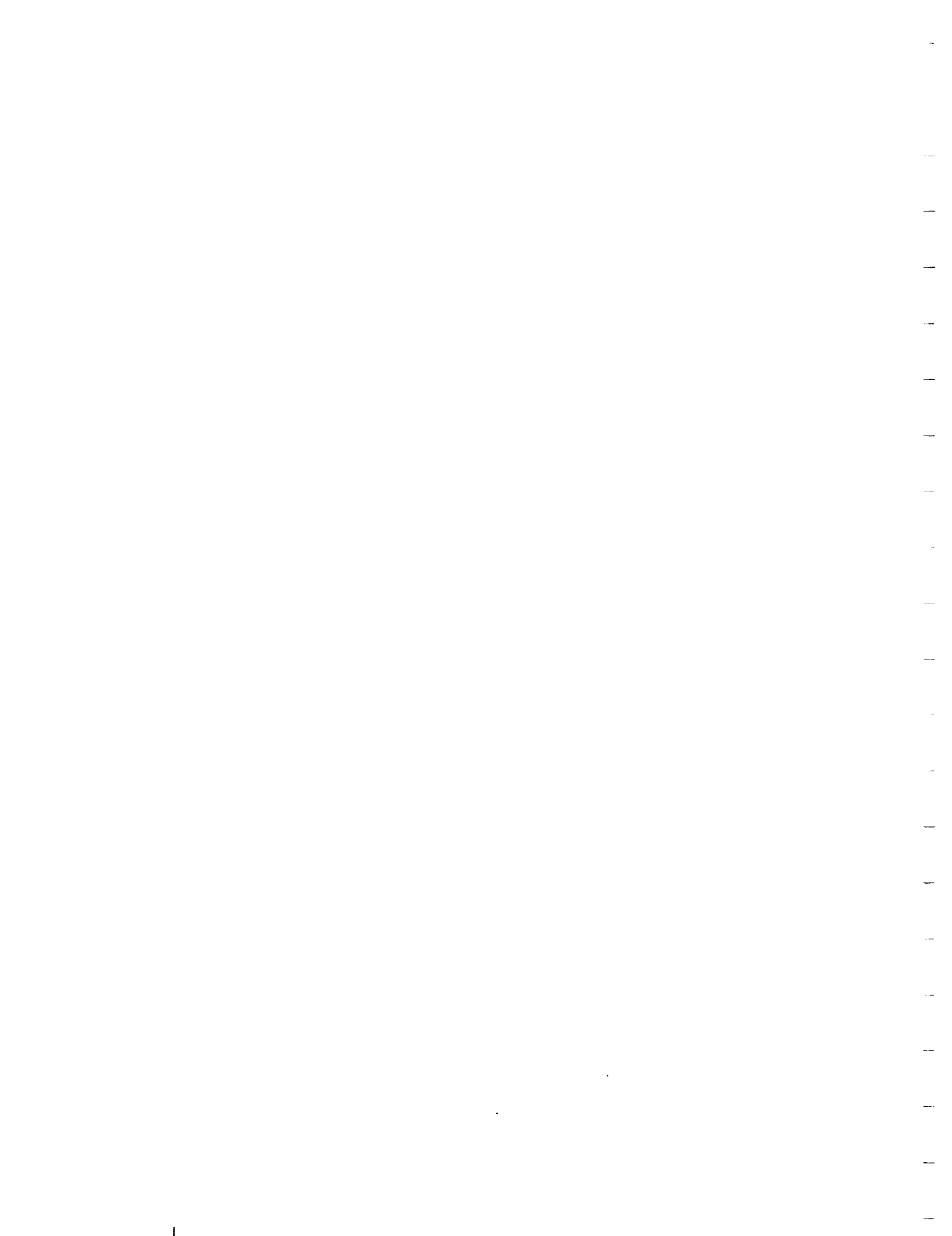
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INTRODUCTION

Atomic hydrogen is capable of entering steel and many other metals and alloys, and when it does, any of several undesirable phenomena may occur which are collectively referred to as hydrogen embrittlement.

Hydrogen can be acquired by most metals in the molten state during manufacture, and most of it can be retained after solidification. However, there usually is a sharp drop in the solubility of hydrogen in a metal when the metal freezes, at least for the high-strength structural materials of interest in this program. Thus, hydrogen may be rejected by the newly solidified metal and tend to concentrate in the remaining liquid. This leads to gas-porosity problems, particularly in castings. As solid metals such as iron, nickel, and alpha titanium cool, the solubility of hydrogen decreases with decreasing temperature. Also, when austenite (gamma iron) transforms to ferrite (alpha iron) or beta titanium transforms to alpha titanium on cooling, there is another sharp drop in solubility. This behavior leads to hydrogen segregation to, and precipitation in, voids or discontinuities, such as microshrinkage cavities or gas holes, during cooling of the solidified metal. As a result of this type of segregation, steel ingots or the billets and forgings produced from them are subject to the formation of flakes or fisheyes, both unwanted defects. This problem is most prevalent in large steel sections (for example, large forgings) or in smaller steel sections that are cooled too rapidly for much hydrogen to effuse from the piece and in which transformation stresses are high (for example, in railroad rails if they are not cooled slowly). Also, at elevated temperatures, hydrogen may react with and remove sufficient carbon from steel so that the material is permanently weakened and is no longer capable of supporting the design stress. Although these are problems of great concern to some steel users, they are relatively unimportant to aircraft and missile manufacturers, and they are not a part of the present program. Therefore, these aspects of hydrogen in steel are not discussed in this review.

This review deals primarily with the loss in mechanical properties experienced by high-strength iron-base and nickel-base alloys and by titanium as a result of hydrogen introduced into the material during manufacturing and processing of the alloy, or in service. Of greatest interest in the present program is hydrogen introduced by pickling, cleaning, and electroplating operations. As a result of the introduction of hydrogen into the alloy, frequently, but by no means always, there is a loss in ductility (particularly in reduction of area) which can be detected in a standard tensile test. However, no embrittlement of the iron-base and nickel-base alloys is detected under conditions of impact loading, such as in a notched-bar impact test. In other instances, the condition cannot be detected in a tensile test but is made manifest as a loss in ability to support a sustained load. The condition is revealed at very low strain rates or under conditions of sustained (or static) loading when hydrogen is present and when a stress gradient or a hydrogen-concentration gradient also is present. When the proper combination of conditions exists, fracture of the metal occurs with little or no evidence of

ductility and at sustained loads that are only a fraction of the yield strength of the non-hydrogenated material. In this program, it is only this catastrophic, brittle failure of structural materials at relatively low applied stresses that is of interest. Although this delayed-failure phenomenon frequently is called "hydrogen embrittlement", some investigators prefer the term "hydrogen-induced, delayed brittle failure" or "hydrogen-stress cracking", since a loss of ductility as measured in the tensile test is not necessarily associated with the condition. The latter term frequently will be used in this review.

The objectives of this program, Contract No. NAS 8-20029, are (1) to determine the susceptibility of specified materials to hydrogen-stress cracking, with particular attention being given to the susceptibility to hydrogen-stress cracking induced by various commonly used cleaning, pickling, and electroplating processes, and (2) to determine the effectiveness of various hydrogen-embrittlement relief treatments. The alloys to be evaluated in the program and the strength levels at which they are to be used are listed in Table 1.

TABLE 1. ALLOYS TO BE STUDIED AND STRENGTH LEVELS AT WHICH THEY WILL BE EVALUATED

Alloy	Ultimate Tensile Strength, psi
Ti-6Al-4V	160,000
AISI Type H-11 steel	260,000
AISI 4130 steel	180,000
AISI 8740 steel	180,000
18Ni maraging steel	260,000
Alloy 718 ^(a)	180,000
U-212 steel	180,000
René 41	200,000
Waspaloy	260,000
17-7 PH stainless steel	200,000 (RH 1075)
17-4 PH stainless steel	200,000 (H-900) ^(b)
AM-355 stainless steel	190,000 (SCT 1000)
AISI 4340 steel	260,000
AISI Type 410 stainless steel	180,000

(a) Alloy 718 is a nickel-base alloy that has the following nominal composition: 19 Cr, 3 Mo, 5 Cb, 0.8 Ti, 0.6 Al, 18 Fe, balance Ni. It was developed by the International Nickel Company and was first designated as Inconel 718. Other manufacturers licensed to produce the alloy have used other trade names, such as Lescalloy 718, Udimet 718, Allvac 718, FS-718, and Unitemp 718. There also may be other trade designations.

(b) Changed from RH 900, 210,000-psi ultimate tensile strength.

The program consists of two parts. One part is a limited survey of the technical literature and current industrial research activities, the results of which have been used to prepare this review of information on hydrogen embrittlement. The other part is a research program involving evaluation of the susceptibilities to hydrogen-stress cracking of the alloys of interest, including susceptibility induced by commonly used cleaning, pickling, and electroplating processes, and an evaluation of the effectiveness of currently used hydrogen-embrittlement relief treatments.

This report was prepared by Battelle Memorial Institute under Contract Number NAS 8-20029, "Study of Hydrogen Embrittlement of Various Alloys", for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. This work was administered under the technical direction of the Propulsion and Vehicle Engineering Laboratory, Materials Division of the George C. Marshall Space Flight Center, with James R. Lowery acting as project manager.

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Three reports(1,2,3)* and one memorandum(4) issued by the Defense Metals Information Center provide a comprehensive review of information published on the general subject of the hydrogen embrittlement of steel through 1962, and NASA personnel agreed that those reports should serve as the background for the survey. Thus, those portions of the reports that bear on the present program are summarized in this review of hydrogen embrittlement, and that information is supplemented by more recent information.

REVIEW OF DMIC PUBLICATIONS ON THE HYDROGEN EMBRITTELEMENT OF STEEL

Effects of Hydrogen on the Mechanical Properties of Steel

The presence of hydrogen affects the mechanical behavior of iron and steel, principally by reducing the ductility (embrittlement), lowering the fracture stress, and causing delayed, brittle failure under suitable conditions.

Apparently, the yield strength of steel is not affected by the presence of hydrogen, which behavior suggests that hydrogen embrittlement does not occur until the yield point is passed. The behavior of ultrahigh-strength steels in which hydrogen-stress cracking has occurred at applied stresses as low as 5 per cent of the nominal ultimate tensile strength might cause one to question this concept. However, very precise measurements of elastic limit in recent years have shown that permanent plastic deformation can take place in as-hardened steels at very low levels of applied stress (elastic limits in the range of 20,000 to 60,000 psi for a wide variety of steels). Various investigators have shown that charging a steel with hydrogen does not affect its hardness. The presence of hydrogen frequently has no effect on the ultimate tensile strength of lower strength steels, but in the case of high-strength steels, the tensile strength is reduced. If, because of decreased ductility, the steel cannot achieve its maximum tensile strength before the fracture strength is reached, the ultimate tensile strength is lowered. The presence of hydrogen has lowered the tensile strength of certain materials to as little as 17 percent of the value for the corresponding uncharged material. In all instances, the fracture strength, or true breaking stress, is reduced by hydrogen. The true stress-true strain curves of hydrogen-bearing and hydrogen-free steel can be superimposed up to the point of fracture of the hydrogen-bearing material. Both the elongation and reduction of area are reduced with increasing hydrogen content. However, so long as permanent damage has not occurred, the ductility can be restored by a suitable aging treatment prior to tensile testing. In ultrahigh-strength steels, a small amount of hydrogen is sufficient to reduce the ductility to essentially zero.

Test temperature has a marked effect on embrittlement due to hydrogen. Hydrogen embrittlement is most severe at intermediate temperatures (generally in the range from -150 F to +210 F). Hydrogen has relatively little effect at the temperature of liquid nitrogen (-321 F) or below, and for ferritic or martensitic steels, the effect drops off rapidly as the temperature is increased above room temperature.

*References are listed at the end of this report on pages 68 through 76.

It is well established that hydrogen embrittlement is sensitive to strain rate. At very high strain rates, on the order of 10 in./in./min and above, the embrittling effects of hydrogen in steel are minimized. Thus, hydrogen embrittlement is a low-strain-rate phenomenon. This strain-rate effect indicates why hydrogen embrittlement of steel has not been detected in impact tests. In general, the notched-bar impact values of steel are not reduced by the presence of hydrogen in the steel, and generally the impact transition temperature is virtually unaffected. If the impact properties are affected, this is evidence that permanent damage has occurred.

Usually, with the more conventional embrittling reactions in ferritic and martensitic steels, the loss in ductility is increased by increased strain rate and by lower temperatures. However, hydrogen embrittlement is promoted by low strain rates and medium temperatures.

Hydrogen embrittlement often manifests itself in the form of delayed, brittle failures which are characterized by fracture at relatively low applied loads, often under static conditions after previously having withstood much higher loads and dynamic conditions as well. High-strength heat-treated steel parts are especially susceptible to delayed, brittle failure induced by hydrogen.

The Main Factors in the Hydrogen-Stress Cracking of Steel

High-strength ferritic or martensitic steel which is subjected to a tensile stress exceeding some critical value (which depends on the strength level of the steel) and which contains hydrogen that is free to move, is susceptible to hydrogen-stress cracking. The problem is especially serious because the minimum stress at which failure will occur decreases as the strength of the steel is increased and because these failures occur with no evidence of ductility, even though in a tensile test the material may exhibit normal ductility. Recovery of ductility (as measured in a tensile test) by removal of most of the hydrogen is no guarantee that the steel will not be susceptible to delayed, brittle failure on static loading if notches or bending stresses are present.

The occurrence of hydrogen-stress cracking depends on the hydrogen content of the steel, and the way in which the hydrogen gets into the steel apparently is of no importance. Such brittle failures do not occur if hydrogen is kept out of the steel or is removed before the steel is damaged permanently. Normally, the critical amount of hydrogen required to induce failure is not present at the sites where failure initiates; hydrogen must move to these sites, either as the result of a hydrogen-concentration gradient or a stress gradient. The former condition exists when the steel is exposed to an environment which permits hydrogen to enter its surface. Stress gradients that will cause hydrogen to move to regions of high tensile stress may result from bending or notches.

Under most conditions, the strength level of the steel is the most important factor affecting the occurrence of delayed, brittle failure (other than the presence of hydrogen in the steel). Both the minimum applied stress that will result in hydrogen-stress cracking and the time required for failure to occur decrease as the tensile strength of the steel is increased.

These failures occur in all types of steel microstructures except austenite. Alloy composition appears to be a relatively unimportant factor in the hydrogen-stress cracking of body-centered cubic steels.

Since this type of failure involves time for the diffusion of hydrogen, it occurs under low-strain-rate or static-load conditions. It has been shown that crack propagation is not a continuous process but consists of a series of individual crack initiations and propagations. Both the incubation period and the propagation of the crack are controlled by the diffusion of hydrogen. However, the mechanism by which hydrogen reduces the ductility of steel and lowers its load-carrying ability still is not known. All of the theories advanced to explain the observed behavior depend on a critical combination of hydrogen and stress.

Hydrogen Content

In steel, and many other metals as well, severe embrittlement can result from very small amounts of hydrogen. The amount to cause cracking in steel can be less than 0.0001 weight per cent or 1 part per million by weight (ppm) average hydrogen content. One report has indicated that an average hydrogen content of less than 0.2 ppm resulted in hydrogen-stress cracking of ultrahigh-strength AISI 4340 steel.

Ferrous alloys will absorb hydrogen only when it is in the atomic form, but certain other metals, such as titanium, will react with molecular hydrogen. Hydrogen can be introduced into the material during melting, heat treating, cleaning, pickling, and electroplating, or it may be picked up as a by-product of certain corrosion reactions. Unless special precautionary measures have been taken to minimize hydrogen pickup during processing, to remove that which was picked up, and to avoid hydrogen pickup in service, most parts will contain appreciable amounts of hydrogen.

The maximum amount of hydrogen that can be introduced into ferritic or martensitic steels without resorting to cold work is on the order of 12 or 15 ppm. Because of the very small amounts of hydrogen with which one must deal in the analysis of steel for hydrogen, the analysis is difficult to perform. Also, since hydrogen diffuses rapidly in body-centered cubic iron and steel at room temperature, it will effuse from such materials at an appreciable rate at room temperature if it is present in more than the equilibrium concentration. This leads to problems in sampling and analysis, for hydrogen may effuse from a newly fractured surface before an effective analysis can be obtained. Thus, the analysis should be performed immediately after the conclusion of an experiment or test, or else the sample should be cooled immediately to a very low temperature where the diffusion rate is negligible and held there until the analysis can be performed.

There is a strong tendency for hydrogen to be distributed nonuniformly in steel. As would be expected, the distribution is nonuniform during periods of hydrogen absorption or effusion. In addition, segregation of hydrogen may occur in a steel part without any change in the total hydrogen content. Because hydrogen is more soluble in austenite than in ferrite, it tends to concentrate in residual austenite. Also, hydrogen tends to precipitate as molecular hydrogen in voids or discontinuities, and this precipitation can continue against large pressures of molecular hydrogen. Thus, it is difficult to relate hydrogen content to the problem of susceptibility to delayed, brittle failure.

Because of these problems in sampling and analysis, many research investigators studying the effect of hydrogen on steel have been forced to use the indirect approach and inductive reasoning. Instead of depending upon an analysis for hydrogen, they have had to rely upon electrolytic charging of specimens with hydrogen under standardized conditions, or heating in a hydrogen atmosphere at a fixed temperature and hydrogen pressure, to introduce fairly reproducible amounts of hydrogen into the steel. Even these approaches are not without hazard, for recent work has shown that variations in the preparation of the steel surface have considerable influence on the rate at which the surface absorbs hydrogen. For example, a very thin cold-worked layer or very thin oxide films have a pronounced effect on hydrogen entry.

The solubility of hydrogen in iron and steel affects the entry of hydrogen into the material and its movement through the metal. The solubility also serves to indicate the magnitude of the concentration gradients that can be expected. At room temperature, the solubility of hydrogen in alpha-iron is very small (a few ppm), but the solubility increases with increasing temperature. A marked increase in solubility accompanies the transformation from body-centered cubic (alpha) iron to the face-centered cubic (gamma) form on heating; that is, the solubility is much higher in austenite than it is in ferrite. The amount of hydrogen present at equilibrium generally is proportional to the square root of the external partial pressure of molecular hydrogen.

Alloying elements have some effect on the solubility of hydrogen in steel, but the crystal structure has a far greater effect.

The following comments apply for solid metals at elevated temperatures, generally above 600 or 750 F. The solubility of hydrogen in nickel is several times greater than that for iron. In general, the solubility in iron-nickel alloys is intermediate to that in iron and in nickel. The solubility in chromium appears to be considerably lower than it is in iron. Many iron-nickel-chromium alloys have solubilities not too different than that for iron. However, the solubility in austenitic stainless steel is high and about like that for nickel, whereas the solubility in a ferritic high-chromium stainless steel is much lower. The solubility in annealed mild steels and annealed low-alloy steels is similar to that for iron.

The effect of composition on solubility at room temperature is not so clear cut, because it is difficult to measure the solubility there. Nearly all investigators have obtained abnormally high solubilities of diffusible hydrogen in iron and mild steels at temperatures below about 750 F as compared with the extrapolation of data for alpha-iron at higher temperatures. There is strong evidence for the existence of traps in annealed material (as well as in cold-worked material) to account for the extra solubility. However, there is no general agreement as to the nature of these traps. In this low-temperature range, austenitic materials have higher solubilities for hydrogen than do the ferritic or martensitic materials, just as at higher temperatures.

A number of investigators have shown that cold work or subsequent annealing have little or no effect on hydrogen solubility in high-purity iron. However, in the case of SAE 1020 steel, for example, cold work may increase the solubility for hydrogen by a factor of as much as 100 or more for some conditions. Variations from this behavior have been reported, and there is no general agreement on the trends. Considerable evidence suggests that the presence of inclusions is necessary for this effect to be observed. If the many data exhibit a general trend, it seems to be that cold work increases the solubility of ferrous materials for hydrogen, and this is generally explained by hypothesizing the existence of traps.

A number of early investigations of the hydrogen-stress cracking of high-strength steels clearly demonstrated that there is a definite correlation between the presence of hydrogen and delayed brittle failures of these materials. For example, compare the data for the specimens charged with hydrogen with those for the corresponding uncharged specimens in Figure 1.

Numerous investigators have studied the effects of variations in hydrogen content. The problems in hydrogen analysis are very great as a result of the small amount of hydrogen usually present and the great mobility of hydrogen in metals, even at room temperature. Therefore, many of the investigations relied largely upon such criteria as variations in cathodic charging time, variations in current density, variations in aging time after charging, or variations in the concentration of, or time of exposure to, nonelectrolytic liquid environments (usually acids) as the basis for evaluating the effects of variations in hydrogen content. Some investigators supplemented these results with warm-extraction or vacuum-fusion analyses for hydrogen. Although hydrogen has been introduced into steel in many ways and under a large variety of conditions, the results of the various investigations nearly all concur in showing that the delayed brittle failures depend directly on the hydrogen content. If the hydrogen can be kept out or removed from the steel before the part is subjected to conditions which result in permanent damage, there is no problem of hydrogen-stress cracking or hydrogen embrittlement. However, this is not easily accomplished, because numerous processing and service conditions are potential sources of hydrogen and because very small amounts of hydrogen (average contents even less than 1 ppm) can induce failure.

Detailed studies of hydrogen-stress cracking have been performed at Battelle Memorial Institute and Case Institute of Technology. At Battelle, unnotched specimens were continuously charged while under static load, and different electrolytes and different current densities were used to produce different hydrogen contents in the steel. In the Case studies, precharged notched specimens were aged for various times at an elevated temperature to produce different hydrogen contents. Both approaches gave longer failure times with conditions that should result in lower hydrogen contents.

Hydrogen Movement in Steel

It has been amply demonstrated that hydrogen-stress cracking occurs in high-strength steel when a critical combination of applied stress, hydrogen content, and time is exceeded, provided that the conditions are such as to permit the hydrogen in the steel to move freely. It is essential that the critical combination of applied stress and hydrogen content be present at a region where failures can be initiated, usually in a region of triaxial stress state. Frequently, the necessary amount of hydrogen is not present at such a site, so movement of hydrogen must take place if failure is to be initiated. Also, as the failure propagates, the region of triaxial stress moves, so, in most instances, hydrogen must move if propagation is to continue. However, hydrogen diffuses readily in ferritic and martensitic steels, but not in austenitic steels, at room temperature, either in response to a hydrogen-concentration gradient or a stress gradient.

One of the unusual characteristics of hydrogen embrittlement is that the embrittlement disappears at low and high test temperatures and is, therefore, most severe in an intermediate temperature range in the general vicinity of room temperature. The disappearance of hydrogen embrittlement at -321 F (liquid-nitrogen temperature) in

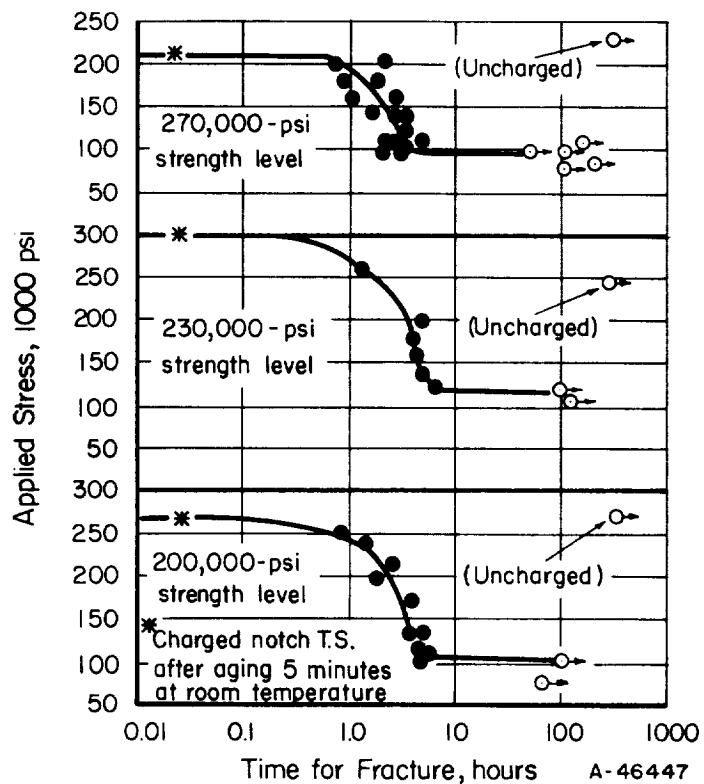


FIGURE 1. DELAYED-FAILURE TESTS ON SAE-AISI 4340 STEEL HEAT TREATED TO SEVERAL STRENGTH LEVELS, SHOWING THE EFFECT OF HYDROGEN⁽⁵⁾

Fixed charging conditions, aged 5 minutes, sharp-notch specimens.

Case Institute of Technology Charging Condition A:

Electrolyte: 4 percent H_2SO_4 in water

Poison: None

Current density: 20 ma/in.²

Charging time: 5 minutes

Aging time: Measured from end of charging to start of test.

SAE 4340 steel heat treated so as to have an ultimate tensile strength of 230,000 psi is illustrated by the data in Table 2.

TABLE 2. EFFECT OF CHARGING CONDITIONS AND TEST TEMPERATURE ON THE DUCTILITY OF UNNOTCHED SAE 4340 SPECIMENS^{(a)(6)}

Condition	Test Temperature, F	Reduction in Area, per cent
Uncharged specimen	Room	40
Specimen charged and cadmium plated	Room	5
Specimen charged and cadmium plated, baked 1 hour at 300 F	Room	10
Uncharged specimen	-321	22
Specimen charged and cadmium plated, baked 1 hour at 300 F	-321	22

(a) Heat treated to 230,000-psi tensile strength.

For most embrittling reactions, the severity of embrittlement generally increases with increasing strain rate. However, for hydrogen embrittlement, the reverse is true for all temperatures at which hydrogen embrittlement is observed. Therefore, hydrogen embrittlement sometimes is called low-strain-rate embrittlement. Hydrogen embrittlement of high-strength steel is nil in an impact test. It may or may not be detected in a standard tensile test of unnotched specimens, depending on the hydrogen content and distribution; however, it is more apparent in a notched tensile specimen with the triaxial stress state introduced by the notch. The most sensitive test for hydrogen embrittlement is the static-loading test of a notched specimen. According to the generally accepted mechanisms for hydrogen embrittlement and delayed, brittle fracture, the strain-rate dependence of hydrogen embrittlement reflects differences in the time available for hydrogen to diffuse into the highly stressed regions. In a test at high strain rates, such as an impact test, the time is not sufficient to permit a damaging amount of hydrogen to diffuse into the region of maximum triaxiality, and embrittlement does not develop. However, as the strain rate is decreased, more hydrogen can diffuse into the highly stressed region, and embrittlement tends to occur. The ultimate in this direction is achieved in the static-loading test where the strain rate is zero. Hydrogen diffuses very rapidly in ferritic or martensitic steels at room temperature, in fact, faster than most intermetallic diffusion at temperatures approaching the melting point of the solvent metal. Therefore, although the phenomenon is diffusion controlled, under many conditions severe embrittlement can be detected in an ordinary tensile test where the crosshead speed may be about 0.05 inch per minute and the test time may be in the neighborhood of 2 minutes. Thus, the accepted mechanism for hydrogen embrittlement is in agreement with the observed effects of temperature and strain rate.

Use of the static-loading test, the only satisfactory way to study hydrogen-stress cracking, precludes a study of variations in strain rate. However, variations in strain rate frequently have considerable effect on other (less sensitive) indicators of hydrogen embrittlement. The effects of variation in strain rate on the ductility of charged and uncharged specimens of mild steel are shown in Figure 2. This figure also shows the temperature dependence of hydrogen embrittlement. Figure 3 shows the effect of

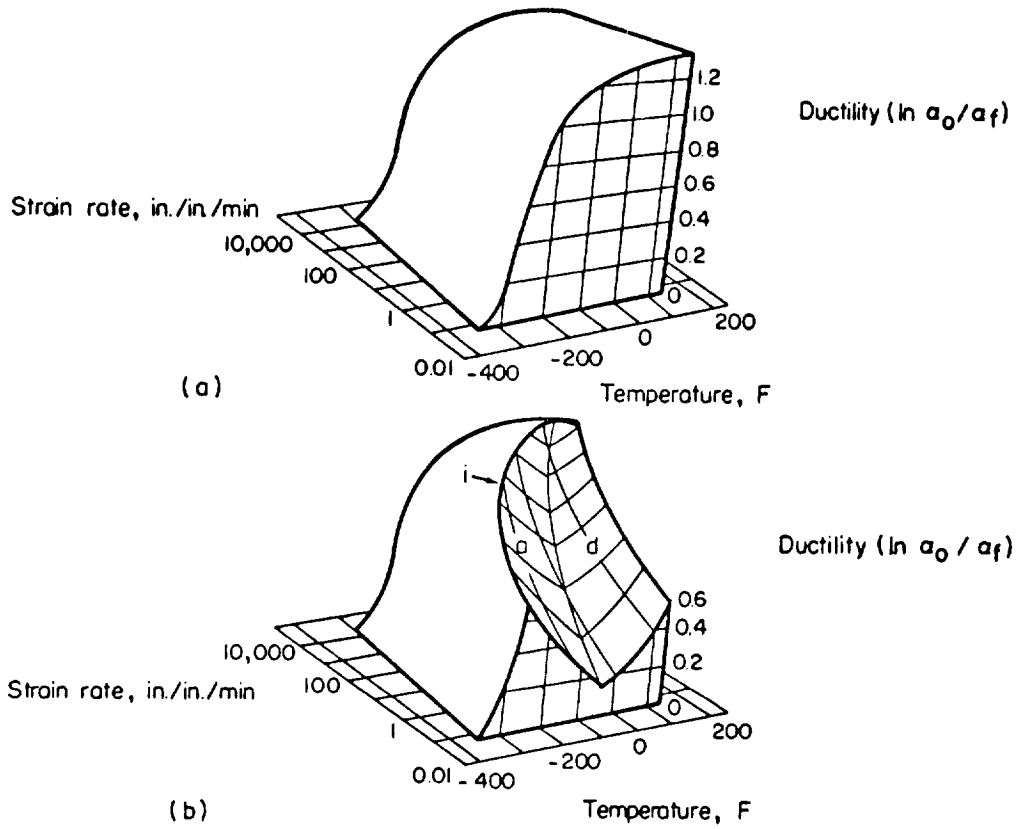
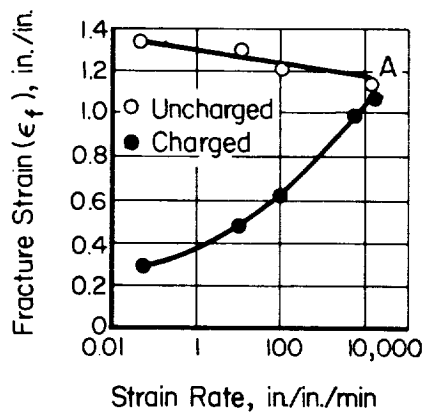


FIGURE 2. THE DUCTILITY OF AN SAE 1020 STEEL AS A FUNCTION OF STRAIN RATE AND TEMPERATURE⁽⁷⁾

- (a) As annealed.
 - (b) As charged cathodically for 1 hr in 4 percent sulfuric acid.
- Curve i, in Figure 63b, bounds the range of strain rates and temperatures where embrittlement is found.



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FIGURE 3. FRACTURE STRAIN AS A FUNCTION OF STRAIN RATE IN A CHARGED AND UNCHARGED, SPHEROIDIZED SAE 1020 STEEL AT ROOM TEMPERATURE⁽⁸⁾

variations in strain rate on fracture strain in charged and uncharged specimens of SAE 1020 steel. Using notched tensile strength as a measure of embrittlement, the data for the experiments with high-strength steel summarized in Table 3 showed that the embrittlement was quite sensitive to small variations in strain rate. However, the results of other investigations have shown that delayed failures can be encountered under conditions for which full recovery is indicated by the conventional tensile test of notched specimens. In other work, the notched tensile strength of hydrogen-charged specimens was much lower as determined by the delayed-failure test (static loading) than as determined by even the slowest of the tensile tests.

TABLE 3. EFFECT OF STRAIN RATE ON NOTCHED TENSILE STRENGTH OF SAE 4340 STEEL AT THE 230,000-PSI STRENGTH LEVEL, CATHODICALLY CHARGED^(a) AND AGED 24 HOURS AT ROOM TEMPERATURE⁽⁹⁾

Nominal Strain Rate (Crosshead Speed), in. /min	Total Time of Test, min	Time From 80,000 Psi to Maximum Load, min	Notched Tensile Strength, psi
0.07	1.75	0.75	301,000
0.05	2.5	1.75	262,000
0.002	47.0	20.0	200,000

(a) Case Institute of Technology Charging Condition A:

Electrolyte : 4 per cent H₂SO₄ in water

Poison : None

Current density: 20 ma/in.²

Charging time : 5 minutes.

Regarding the movement of hydrogen in steel, the overall process from bulk gas phase on one side of the metal, through the metal, to the bulk gas phase on the other side is termed permeation. This consists of interactions at both the entry and the exit surfaces of the metal, as well as the actual transport through the metal. The term diffusion strictly applies only to transport through the metal. In the usual experiment with hydrogen, the permeation, rather than diffusion, is measured, because one is dealing with the overall driving force of gas pressure and because there are problems of analysis for hydrogen as discussed previously which make it difficult to obtain the hydrogen contents of a succession of individual slices or layers as is required to determine the diffusion coefficient.

Permeability depends on the temperature, the nature of the metal, the boundary conditions, and the thickness of the iron or steel. The boundary conditions include the nature of the steel surface and such things as the type and concentration of the acid in contact with one side of the steel diaphragm in pickling, the partial pressure of hydrogen in the gas used in pressure charging, the nature of the electrolyte and the current density in cathodic charging from one surface, and the environment surrounding the exit surface. The presence or absence of a poison in pickling or in cathodic charging is a very important factor. Thus, many variables affect the rate at which hydrogen permeates steel, and, since apparently conflicting results have been obtained, the process is not yet completely understood.

A number of investigators have measured the amount of hydrogen (P) permeating from the gas phase through a thin tube, and they have found that the following equation

describes the observed behavior:

$$P = Kp^{1/2}e^{-B/T} \quad , \quad (1)$$

where p is the pressure, T is the absolute temperature, and K and B are constants. The permeation rate of hydrogen through steel is approximately proportional to the square root of the pressure (except at very low pressures); this behavior indicates that it is only atomic hydrogen that penetrates steel and diffuses through it. However, one investigator has found that for many steels the permeation rate becomes a constant when a hydrogen pressure of about 100 atmospheres is reached. Variations in pressure primarily affect hydrogen entry into steel, whereas the greatest effect of temperature on permeation is through its effect on diffusion.

The permeability, P , is related to the solubility, S , and the diffusivity, D , as follows:

$$P = S \cdot D \quad . \quad (2)$$

This relationship holds only for the case where the diffusion through the bulk metal is the controlling rate, and surface resistances to permeation are negligible. It has been shown that these three properties are mutually consistent for hydrogen permeating through iron or steel at temperatures above about 750 F. However, this relationship does not describe the observed behavior at lower temperatures, apparently because surface reactions related to hydrogen entry are the rate-controlling factors in permeation in this lower temperature range.

Because of the great number of factors that influence permeation, the analysis of the results is complicated. However, the person interested in hydrogen-stress cracking usually is concerned with hydrogen entry, hydrogen diffusion through the bulk solid, and the removal of hydrogen, the processes of which permeation is comprised.

Hydrogen Entry

Hydrogen enters steel only when it is presented to the steel surface as atomic hydrogen. Those ways in which hydrogen enters steel subsequent to its manufacture are of greatest interest to the person concerned with hydrogen embrittlement and hydrogen-stress cracking. The principal means of hydrogen entry are corrosion (including pickling), electrolytic processes, and exposure to hydrogen gas at elevated temperatures or pressures.

Atomic hydrogen can be liberated at the surface of iron or steel as a result of direct attack by corrosive media or galvanic corrosion. Important examples of the former are acid attack as in acid pickling, attack by hydrogen sulfide, and corrosion by water such as has resulted in hydrogen-stress cracking of pressure vessels being pressure tested with water. In galvanic corrosion, where two dissimilar metals are joined electrically in the same corroding medium, atomic hydrogen may be evolved on iron or steel when it is the more noble metal, for example, when it is coupled with an active metal such as magnesium, aluminum, or cadmium.

Pickling in an acid solution frequently is used to remove mill scale or rust from steel before applying a metallic coating or paint. The corrosion that occurs releases atomic hydrogen at local cathodes on the steel surface, and a portion of this atomic

hydrogen may enter into the steel. Acid pickling may introduce more hydrogen into steel than is introduced by electroplating operations. Hydrogen embrittlement as the result of acid pickling has been observed in all manner of plain-carbon and low-alloy steels (including alloy steels heat-treated to high strength levels) and in ferritic and martensitic stainless steels.

One method used to reduce destruction of valuable metal, minimize surface roughening, and reduce unnecessary consumption of acid in pickling is to make the workpiece a cathode by means of an external potential source, instead of merely dipping it in the acid. However, cathodic pickling increases the likelihood of introducing hydrogen into the steel. A method of reducing the evolution of hydrogen resulting from attack of the metal is to make the steel the anode during acid pickling. Such anodic pickling should effectively prevent the evolution of hydrogen on the steel, but sometimes the attack of the steel and the acid consumption are increased. The method most frequently used to reduce the problems related to metal attack and hydrogen liberation at the same time is to add to the acid pickling bath a substance that will restrain attack on the metal while still permitting the scale to be undermined; such substances usually are called inhibitors. Nitric acid, an oxidizing acid, has been regarded as causing no hydrogenation of steel, even though most of the base metals that liberate hydrogen from hydrochloric acid are attacked also by nitric acid. However, it has been found recently that under some conditions treatment of steel with nitric acid can introduce hydrogen into the steel. Some investigators working with mild steel have found that cold working of the steel markedly increased both the absorption rate and the amount of hydrogen that could be absorbed during pickling.

Another source of hydrogen in steel is the corrosion of steel in aqueous environments. Exposure to water vapor or superheated steam also introduces hydrogen into steel. Steel has been found to pick up hydrogen from a hydrocarbon lubricant, and nonaqueous hydrogen-bearing liquids such as a number of common hydrocarbon solvents may at times be a source of hydrogen.

It is rather generally agreed that the phenomenon of sulfide-corrosion cracking of steel is the result of the penetration of atomic hydrogen into the steel. That is, sulfide-corrosion cracking is identical with hydrogen cracking. The only part played by corrosion in this phenomenon seems to be to supply the nascent hydrogen to the surface of the steel. The sulfide ion, being one of the most effective poisons of the hydrogen-recombination reaction, serves not only to corrode the steel and supply the atomic hydrogen, but to make it possible for much of this atomic hydrogen to enter the steel. Sufficient hydrogen to embrittle the steel may be introduced at an insignificant corrosion rate. Both martensitic and ferritic structures fail when the strength level of the steel, the magnitude of the applied stress, and the hydrogen content introduced by sulfide corrosion are high enough, but austenitic materials have not cracked under similar conditions. Water is an essential factor in the corrosion of iron or steel by hydrogen sulfide.

Certain Cr-Mo-Al and Cr-Mo-V steels, when properly heat treated, perform better in severe production service in sour-gas fields (where the gas contains H₂S) than does the conventional API Grade N-80 steel, and the same superiority is exhibited in laboratory sulfide-corrosion tests. A minimum susceptibility to cracking in constructional Cr-Mo-V steels occurs after tempering the steel at elevated temperatures so as to produce a structure of fine spheroidal carbides. Ferritic steels containing about 12 percent chromium are less susceptible to general corrosion than are steels with only

2 percent or so chromium, but they also show sulfide-corrosion cracking when heat treated to high strength levels. A 9 percent nickel steel was particularly susceptible to this type of cracking.

It is possible that protective coatings such as zinc, cadmium, or aluminum may result in the introduction of hydrogen into steel during service. These metals, being more anodic (more active) than steel under most service conditions, tend to protect the steel from corrosion. However, at breaks in the coating, the steel could become a cathode in an electrolytic cell, and this might result in the introduction of hydrogen into the steel. This is one form of galvanic corrosion.

Electroplating, cathodic cleaning, electrolytic machining, and cathodic charging are examples of electrochemical processes which usually introduce hydrogen into steel. Cathodic protection of steel structures, either with sacrificial anodes or with non-sacrificial anodes and an external current, is another source. High hydrogen concentrations can be introduced into steel from these various processes, often with serious consequences. Furthermore, the presence of small amounts of certain elements or compounds in the electrolyte, which are known as cathodic poisons, greatly increases the likelihood that hydrogen will enter the steel. Hydrogen evolved cathodically from alkaline electrolytes, such as NaOH, shows much less ability to enter iron and steel specimens than that evolved from acid electrolytes or neutral solutions.

Some of the variables in the cathodic charging process include specimen thickness, composition and pH of the electrolyte, current density, cathodic poisons and inhibitors, steel structure, and the nature of the steel surface. With either continuous charging or prior charging of notched specimens, the hydrogen content of the specimen may be varied by changing the current density. With prior charging, the hydrogen content also can be varied by using different charging times or by aging or baking for different times to permit different degrees of hydrogen effusion prior to testing. Some effects of variation in current density and in the nature of the electrolyte are illustrated in Figure 4. The effects of a cathodic poison are shown in Figure 5. The first portion of the curve shows the behavior of the steel wire when treated cathodically for 310 minutes in pure 1N H_2SO_4 solution at a current density of 0.15 amp/cm² at a temperature of 37 F. The rate of elongation resulting from hydrogen penetration rose markedly after thiourea was added in the 311th minute. Thiourea is decomposed at the cathode and H_2S is formed which is a powerful cathodic poison which results in increased hydrogen penetration of the steel accompanied by plastic deformation of the wire.

Sufficient hydrogen is introduced into steel during a commercial-type electroplating process to cause substantial embrittlement and to cause hydrogen cracking under many conditions. These effects result from hydrogen that is plated concurrently with the metal, part of the hydrogen being absorbed by the steel. Steel is embrittled by virtually all of the electroplating processes, including cadmium, chromium, zinc, tin, nickel, lead, copper, and silver. This has been a serious problem with high-strength steel parts where the electroplated coating is needed for corrosion resistance and yet its application makes the part susceptible to failure by another mechanism - hydrogen cracking. In addition, the presence of the electroplate makes the removal of hydrogen from the steel much more difficult. Hydrogen introduced into specimens during cadmium electroplating reportedly may be as high as that introduced through severe cathodic charging. Other work has shown that frequently more hydrogen is introduced in acid pickling to remove scale or in cathodic cleaning prior to electroplating than is introduced in the electroplating operation itself. The conventional cyanide bath for

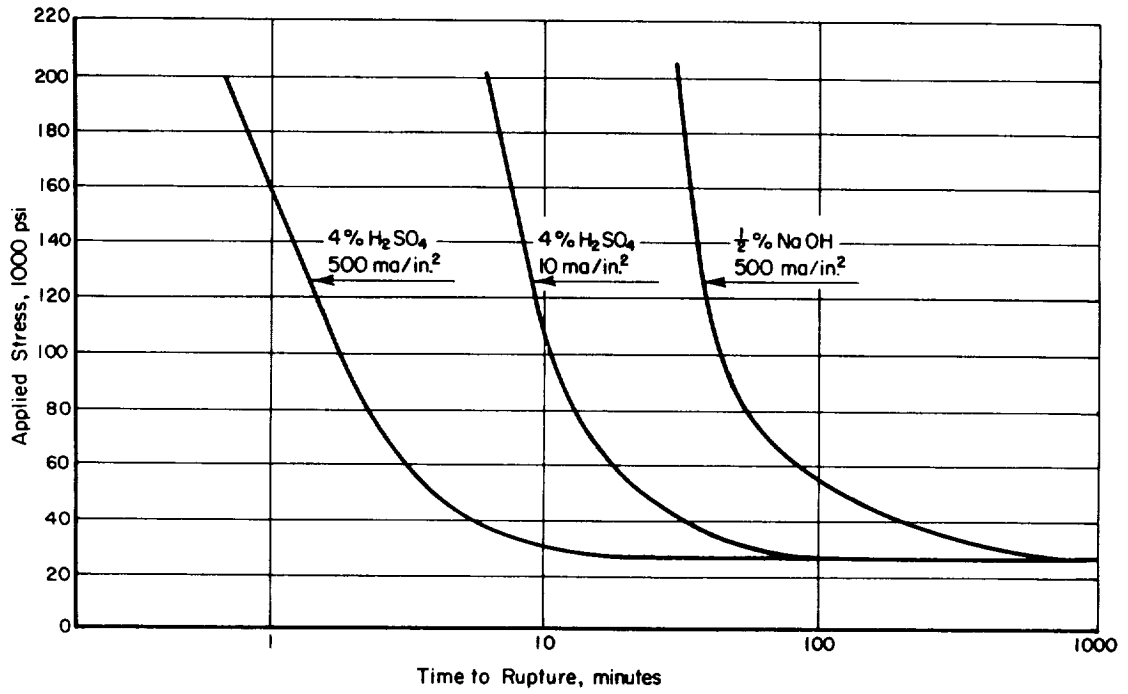


FIGURE 4. TIME FOR FAILURE AS A FUNCTION OF APPLIED STRESS FOR VARIOUS CHARGING CONDITIONS⁽¹⁰⁾

SAE 4340 steel, 230,000-psi ultimate tensile strength.

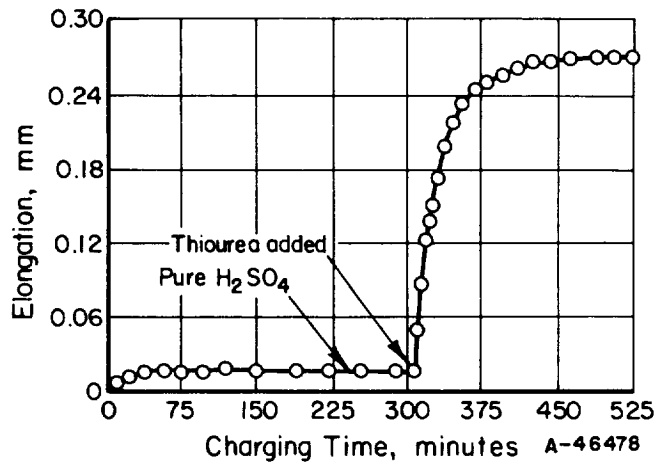


FIGURE 5. ELONGATION OF IRON WIRE AS A FUNCTION OF TIME OF CATHODIC CHARGING, SHOWING EFFECT OF ADDING A CATHODIC POISON⁽¹¹⁾

Original length of wire = 180 mm.

cadmium plating was one of the worst from the standpoint of hydrogen embrittlement. Therefore, many studies of cadmium electroplating processes were carried out to determine if one or more could be used safely for electroplating ultrahigh-strength steel. Some baths tested were found to operate at approximately 100 percent cathode current efficiency (virtually all metal and very little hydrogen deposited). With some high-efficiency baths, no detrimental hydrogen embrittlement occurred when the bath was used without a brightener, but the coatings were granular in appearance. When a grain refiner or brightener was added to the bath, some of specimens plated subsequently failed in the sustained-load test, even when the bath with the brightener had a higher cathode current efficiency than the bath without the brightener. It appeared that the significant difference in the two electrodeposits was in the physical structure. Granular deposits are more porous than are smooth ones, thereby allowing the hydrogen to be driven out to a greater extent during the usual baking treatment after plating, since dense cadmium serves as a barrier to hydrogen. Thus, the residual detrimental hydrogen embrittlement obtained from a cadmium electroplating bath is a function of cathode efficiency, which controls the entry of hydrogen, and of the structure of the coating, which controls the rate of removal of hydrogen during the postplating baking treatment. A suitable porous cadmium plate permits hydrogen effusion while still providing appreciable corrosion protection. Nonelectrolytic coating with cadmium by the vacuum-metallizing technique offers considerable promise in that no hydrogen is deposited during the coating process. However, at least some investigations indicate that the vacuum-metallized cadmium does not serve as a barrier to the subsequent entry of hydrogen, such as might be encountered in service.

Hydrogen can enter steel by other means, two of the more important ones being thermal charging and pressure charging. In pressure charging in hydrogen and in thermal charging in a hydrogen-bearing atmosphere, the driving force for hydrogen entry into steel is the partial pressure of dissociated (atomic) hydrogen. The dissociation of hydrogen is strongly endothermic and, therefore, is promoted by high temperatures. Although the dissociation is very small at room temperature, it becomes appreciable at temperatures used in heat treating steel and even more so at steelmaking temperatures (about 2900 F). In the electric arc, hydrogen may be highly dissociated. Hydrogen is readily picked up by steel in electric-arc welding often leading to weld underbead cracking by the hydrogen-stress-cracking mechanism. Thermal charging is more effective when it is carried out in wet rather than dry hydrogen. Entry of atomic hydrogen into steel at elevated temperatures can result in embrittlement and/or a loss in load-carrying ability. In addition, conditions frequently are such that decarburization of the steel occurs, thought to be the result of the formation of methane (CH_4). Since hydrogen diffuses so readily in steel, this reaction is not limited to the surface layers but can occur throughout the section, thereby weakening the steel even further.

Another aspect of the hydrogen problem in steel involves holding hydrogen at high pressures, especially at somewhat elevated temperatures. The partial pressure of dissociated hydrogen increases with increasing gas pressure, but as the square root of the pressure. Thus, the rate of permeation is expected to be proportional to the square root of the pressure, and this is the behavior observed for iron at elevated temperatures. The solubilities of hydrogen in α -iron obtained by the pressure-charging method at 100-atmospheres pressure of hydrogen gas and various temperatures are as follows⁽¹²⁾:

Temperature		100-Atmosphere Solubility, ppm
C	F	
585	1085	10.98
538	1000	8.08
490	914	6.13
390	734	3.44
290	554	3.19
210	410	2.36
145	293	1.57

Most of the studies of pressure and thermal charging have been related to the attack of carbides by hydrogen at elevated temperatures, which is not a part of the mechanism of hydrogen-stress cracking.

If the entry of hydrogen, rather than diffusion is the controlling factor in permeation of hydrogen through steel, as appears to be the usual case near room temperature, then variations in the nature of the steel surface will influence hydrogen permeation. Roughening the surface increases the area available for adsorption. In one experiment, etching a polished surface increased the permeation rate by a factor of 10. Variations in the mechanical preparation of the surface, such as by grit blasting, vapor blasting, surface grinding, mechanical polishing, and electropolishing, can affect the hydrogen permeation rate considerably. All of the effect is not due to variations in surface roughness; surface activation or poisoning accomplished by exposure to suitable environments also affect adsorption and, hence, hydrogen entry. Chemisorbed films of inhibitors or of cathodic poisons can have a marked effect on hydrogen entry. However, cold work has its effect largely on diffusion and not on hydrogen entry.

Hydrogen Diffusion

Most of the current theories of hydrogen embrittlement and hydrogen-induced delayed brittle failure of steel depend on diffusion of hydrogen in some way. Thus, a proper understanding of these phenomena can be achieved only when the diffusion process itself is properly understood. Although much work has been done recently on the diffusion of hydrogen in steel, the phenomenon still is not completely understood, and certain apparent discrepancies remain to be resolved. Most of the serious discrepancies have been encountered at the lower temperatures in the vicinity of room temperature. This is unfortunate from the standpoint of understanding hydrogen-stress cracking of steel, because this is the temperature range in which this cracking is encountered.

The diffusivity of hydrogen in steel depends primarily upon the temperature, the nature of the steel (including composition, microstructure, and crystal structure), and the amount of hydrogen present in the steel at the time. The driving force for diffusion of hydrogen in steel can be either a hydrogen-concentration gradient or a stress gradient. Most diffusion processes occur in response to a concentration gradient. However, it was shown in studies of hydrogen-stress cracking of steel that hydrogen also can diffuse in response to a stress gradient. For example, in a region of uniform hydrogen content, hydrogen can diffuse to the region of maximum stress just in front of a crack tip in a part under load.

As has been mentioned previously, the values of permeability, solubility, and diffusivity are consistent with the relationship $P = S \cdot D$ at elevated temperatures, but

anomalously high values of solubility arise at lower temperatures. What appear to be anomalously low values of diffusivity (and sometimes permeability) have been observed by a number of investigators at the lower temperatures.

The effect of temperature on the rate of diffusion can generally be expressed by

$$D = k \cdot e^{-Q/RT}, \quad (3)$$

where T is the absolute temperature in degrees Kelvin, Q is the activation energy (calories per gram mole) necessary for diffusion, R is the gas constant (1.987 for the units given), and k is a constant. With these units, D has the units cm^2/sec . Since this theoretical equation that links diffusivity and absolute temperature is exponential in form, a plot of $\log_{10} D$ against $1/T_{\text{abs}}$ (Arrhenius-type plot) should be linear. Because the effect of temperature on permeability is through its effect on diffusivity, a similar relationship would be expected between $1/T$ and the log of the permeability. A linear relationship has been found between $1/T$ and the log of the permeability for temperatures down to the range of about 600 to 400 F for several steels. Many, but not all, investigators have found anomalously low permeability at temperatures below this range. Some have attributed this to a change in the mechanism of permeation, the rate being controlled by diffusion at higher temperatures but by surface processes (entry) at the lower temperatures.

A number of investigations have been made of the diffusivity of hydrogen in iron and steel at room temperature and slightly elevated temperatures, but the various values obtained are in poor agreement. However, nearly all follow the trend for experimentally determined coefficients for temperatures below about 400 F to be considerably lower than would be predicted by extrapolation of high-temperature measurements for α -iron. This observed behavior of hydrogen in ferrite is just the reverse of its behavior in most other metal systems where low-temperature deviations in the diffusion coefficient have been in the direction of higher values than are predicted by extrapolation of high-temperature data. These deviations in metals other than iron or iron alloys have been explained as resulting from preferentially rapid diffusion along grain boundaries or dislocations. The results of two investigations showed that grain boundaries had no appreciable effect on the rate of diffusion of hydrogen through iron. Thus, it is accepted that the penetration of hydrogen into iron occurs throughout the lattice.

The results obtained for the temperature dependence of the diffusivity of hydrogen in α -iron shown in Figure 6 are typical of the generally observed behavior in which anomalously low diffusivity is indicated at the lower temperatures. These results and those of other recent investigations have led to the following conclusions. In the upper temperature region, there appears to be only the interstitial diffusion process with an activation energy of approximately 3000 cal/mole. However, there appear to be two diffusion processes in the lower temperature range. When hydrogen is first introduced into steel, it moves around relatively freely, and the diffusion process has an activation energy of about 3000 cal/mole. But, with the passage of time, the hydrogen appears to be partially trapped by some lattice defect, and the diffusion of this hydrogen takes more energy to become activated (approximately 6000 cal/mole is required) and takes place at a lower rate.

It is especially noteworthy that a big drop in permeability and diffusivity accompanies the α -to- γ transformation on heating, and there is a sharp increase for the reverse transformation on cooling. For a given steel composition, the diffusivity in

austenite is much lower than in ferrite for a given temperature, as is illustrated in Figure 7. One group of investigators found that only when the temperature reaches about 2100 F does the diffusivity in γ -iron reach that determined for α -iron at 1200 F. Another group found the diffusivity in pure γ -iron at 2100 F to correspond to that in pure α -iron at about 900 F, as is shown in Figure 8. This figure also shows the low diffusivity of hydrogen in an austenitic stainless steel. Other investigators measured the permeation rates for a Cr-Ni-W steel over a wide range of temperatures; by extrapolation of the curves obtained, they found the permeation rate at 212 F in the α -condition to be the same as that at 572 F for the γ -modification.

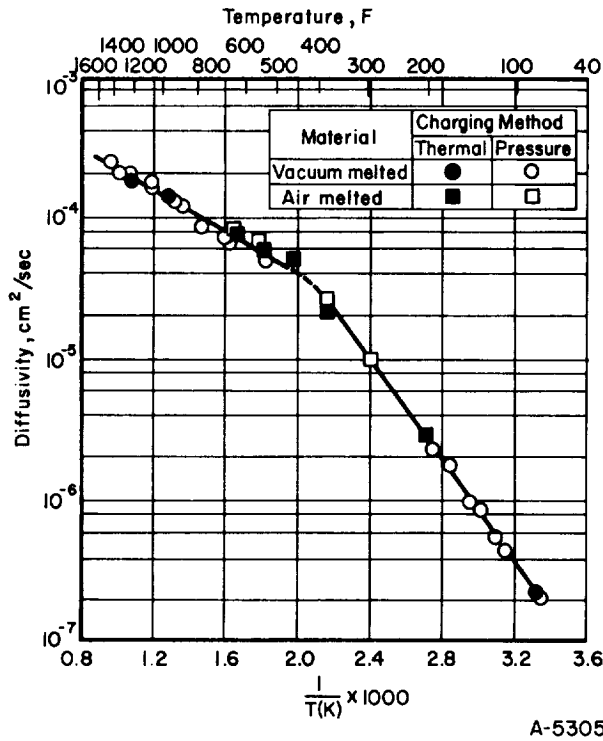


FIGURE 6. TEMPERATURE DEPENDENCE OF THE DIFFUSION COEFFICIENT OF HYDROGEN IN α -IRON⁽¹³⁾

In addition to the effect of crystal structure, Figure 8 illustrates some of the effects of variation in composition on diffusivity of hydrogen. Geller and Sun⁽¹⁵⁾ found that alloy additions of silicon, chromium, or nickel decrease the diffusivity in either the α - or the γ -modification of iron. In measurements at room temperature, these investigators observed much lower hydrogen-evolution rates for a supersaturated alloy containing 4.33 percent silicon than for a 27.45 chromium-iron alloy. Specimens of alloys with 5.34 and 8.0 percent silicon (balance iron) showed no hydrogen evolution at all at room temperature. Other investigators studied the effects of chromium, nickel, and molybdenum on the rate of hydrogen permeation in iron. They found that chromium had little effect on permeation in the γ -range, but greatly reduced the rate of permeation in the α -range (see Figure 9). Nickel and molybdenum had little effect. Very low diffusion rates have been observed for 14 percent chromium, ferritic stainless steel, as is shown by the following comparison⁽¹⁶⁾:

Steel	Approximate Diffusion Constant at Indicated Temperature, cm ² /sec		
	-108 F (-78 C)	Room Temp	212 F (100 C)
2-1/2Ni-Cr-Mo	5.8 x 10 ⁻⁹	3.2 x 10 ⁻⁷	1.34 x 10 ⁻⁵
3Cr-Mo	~2.5 x 10 ⁻⁹	~5.0 x 10 ⁻⁸	--
14Cr	--	~2.8 x 10 ⁻⁹	~3.2 x 10 ⁻⁷

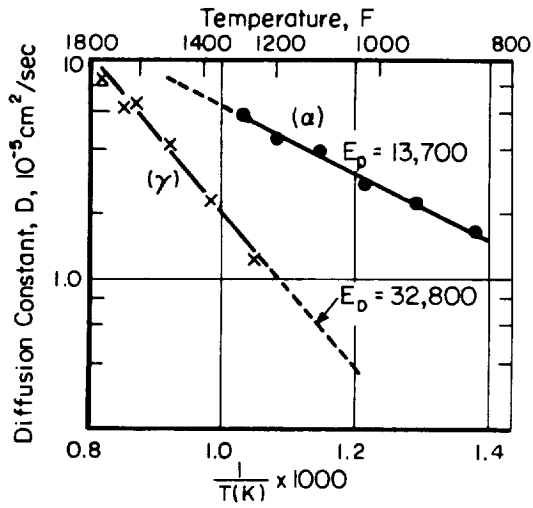


FIGURE 7. DIFFUSION CONSTANT FOR HYDROGEN OBTAINED BY TIME-LAG METHOD FOR IRON-4.36% NICKEL ALLOY⁽¹⁴⁾

Showing the effect of crystal structure on diffusion.

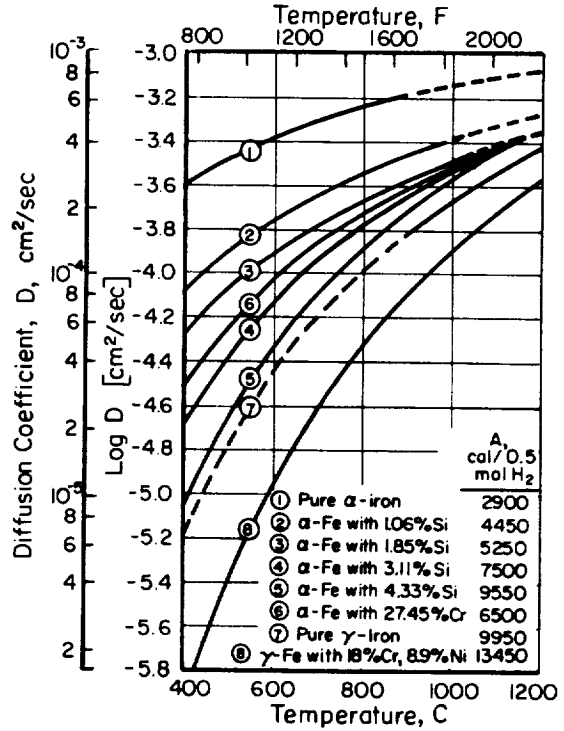


FIGURE 8. DIFFUSION COEFFICIENT OF HYDROGEN IN IRON AS A FUNCTION OF TEMPERATURE, CRYSTAL STRUCTURE, AND ALLOY ADDITION⁽¹⁵⁾

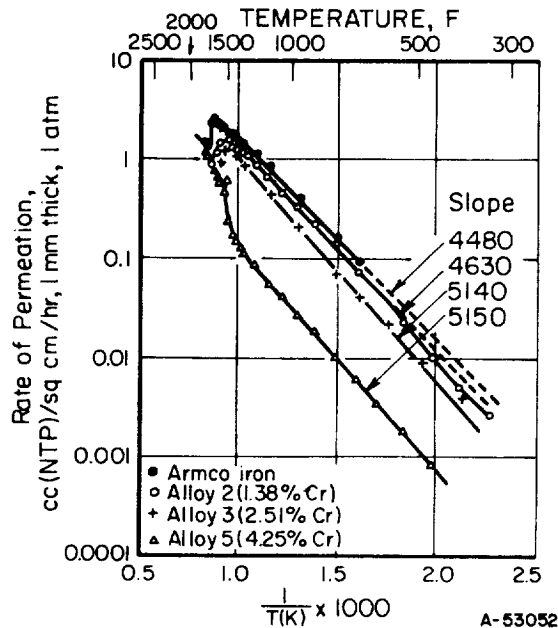


FIGURE 9. PERMEATION ISOBARS OF Fe-Cr ALLOYS⁽¹⁴⁾

The presence of carbon considerably reduces the hydrogen-permeation rate at ordinary temperatures, but at high temperatures, the effect of carbon appears to be just the reverse.

Not only does the presence of carbon have considerable influence on the permeation of hydrogen through iron or steel, but the physical form of the carbide particles (cementite, Fe_3C) exerts a very considerable influence, too. That is, steel microstructure has an important effect on hydrogen permeation. In one investigation, the hydrogen permeation rate was 12 times greater when the cementite was in globular form than when it was in the form of coarse lamellar pearlite. It appears that carbide particles in any form hinder the passage of hydrogen through steel, even after steady-state conditions have been reached. Cementite in the coarse spheroidized form appears to have the least effect on permeability; coarse lamellar pearlite offers more resistance to permeation than does fine pearlite; and martensite, in which the carbon atoms are present in the iron lattice but in which there is considerable strain, exhibits the lowest permeability of all.

If the rate of hydrogen flow is determined by the rate of diffusion, then under given conditions, the permeation should be inversely proportional to the thickness of the metal. Such behavior has been observed at high temperatures. Deviations from this inverse relationship have been observed near room temperature and especially in thin membranes, apparently as the result of surface processes on the entry and exit surfaces which were influencing the permeation rate.

A number of investigators have studied the effects of elastic and plastic deformation on the rate at which hydrogen permeates steel at room temperature, but only a few have studied their effect on the diffusion of hydrogen. It was pointed out previously in this review that controversial opinions exist concerning the effect of cold work upon the occlusion of hydrogen in iron and steel. The results obtained for permeability likewise are controversial. Since the majority of investigators have studied permeation of hydrogen in iron and steel by the steady-state permeation-rate method which depends on solubility and diffusivity, it is to be expected that results obtained for diffusivity would be controversial, too.

In one investigation, cold work accelerated the permeation of hydrogen. However, a number of other investigators found that severe plastic deformation decreased the permeation rate of ferritic steels, although the quantity of hydrogen occluded was markedly increased. In one investigation of a number of ferritic steels, without exception increasing severity of cold work in the range of 0 to 70 percent reduction resulted in a decrease in permeation rate. A decrease by a factor of 10 as the result of about 70 percent reduction in area was not uncommon. However, at least two other groups of investigators concluded that cold work had no effect at all on the permeability, though the maximum amount of hydrogen absorbed and the rate of absorption increased with the amount of cold deformation. In one of these studies, although cold reduction did not alter the permeability, annealing the cold-worked material decreased it by a factor of at least 5. In still another investigation, it was observed that the permeation rate of low-carbon steel first increased with increasing cold work, then passed through a maximum at about 10 to 20 percent cold reduction, and finally decreased rapidly with further deformation; for sheets cold worked 60 to 90 percent, the permeability was nearly zero. Thus, four markedly different behaviors for the effect of cold work on the permeation of hydrogen through steel have been described. Obviously, considerably more work is needed to ascertain the behavior and the factors which affect it.

Recently, the rate of permeation of hydrogen through a highly purified iron was measured over a wide range of temperatures and pressures. No difference was observed in the permeability or the diffusivity between the material as cold reduced 26 percent and the same sample subsequently annealed. This finding would appear to be consistent with the findings of a number of investigators that cold work or subsequent annealing have little or no effect on hydrogen solubility in high-purity iron. It may be that the presence of inclusions is necessary if cold work is to affect either hydrogen solubility or diffusivity. However, in another investigation it was found that the diffusivity in an iron-carbon alloy was decreased manyfold in the temperature range 480 to 750 F by prior cold working, and the effect increased as the severity of cold work increased. Since cold working increased the absorption by about the same factor, the permeability should have remained approximately constant. However, when the samples were strained at -240 F prior to measurement of the diffusivity, the cold deformation had little or no effect on the diffusion coefficient.

Hydrogen Removal

Although under certain corrosive conditions the hydrogen content of steel will increase during storage, in normally dry air hydrogen is constantly being lost from a piece of ferritic or martensitic steel until the hydrogen content of the steel comes to equilibrium with the environment. The rate of loss depends on, and varies greatly with, such factors as temperature, thickness and shape of the material, composition of the steel, whether the steel is ferritic or austenitic, the amount of cold work, the nature of the environment, surface roughness, and surface area.

The loss of hydrogen from an austenitic steel is imperceptible at room temperature. For example, in one investigation no measurable quantity of hydrogen escaped at room temperature from austenitic samples in a period of 3 months, even though they contained 2 to 5 times as much hydrogen as the ferritic samples from which as much as 61 percent of the total hydrogen content was evolved in 10 days. The method of introducing hydrogen into the steel, whether it be pickling, cathodic charging, or heating in hydrogen, has little effect on the rate of removal at room temperature. However, variation in the cross-sectional area of the test piece has a large effect on the rate of removal at both room temperature and elevated temperatures, because the removal depends on the diffusion of hydrogen. For this reason, the rate of hydrogen evolution from all steels increases with increasing temperature, at least within a few hundred degrees of room temperature. The curve in Figure 10 shows the variation with temperature of the heating time required to obtain relief from hydrogen embrittlement, that is, for obtaining near-maximum ductility in the mild steel and for the specimen size used in the study. The marked effects of temperature and the effects of holding time at a given temperature on the residual fraction (U) of hydrogen remaining in the steel in another investigation are shown in Figure 11. Note that two different scales have been used to show the extremes of rate. Based on the time to reach $U = 0.5$ and taking the rate at room temperature as unity, the rate at 392 F was 209 times faster and the rate at -108 F was 1/50 as fast. The results of other investigations indicated that aging to remove hydrogen from ferritic steel is roughly 250 to 500 times faster at 400 F than it is at room temperature, and that the aging time increases as the $3/2$ power of specimen size. This means that the time increases directly with increasing volume and inversely with increase in surface area. Therefore, for a cylindrical bar, the time increases as the square of the diameter. The effects of baking for various times on the susceptibility to delayed brittle failure are shown in Figure 12.

As indicated previously in this review, the solubility of hydrogen in α -iron increases rapidly with increasing temperature. Therefore, baking or aging treatments to remove hydrogen from ferritic steel must be a compromise between greater permeability or rate of diffusion obtained at increased temperatures (so as to shorten the treatment time) and the lower solubility prevailing at lower temperatures. Frequently, a temperature of about 375 to 400 F is used.

Practically all alloy additions to ferrite retard the effusion of hydrogen, but silicon and chromium are especially effective. The effects of silicon and chromium are shown in Figure 13. In another investigation, the time to reach a given residual hydrogen fraction for a 14 percent chromium ferritic steel was approximately 100 times longer than for the 2.5Ni-Cr-Mo steel of Figure 11. Retained austenite has a high equilibrium solubility for hydrogen, so hydrogen tends to concentrate in this constituent. This hydrogen cannot be removed by baking unless the treatment also transforms the retained austenite.

A number of studies have shown that environment is important in the removal of hydrogen from steel. Exposure to hot air saturated with water vapor is more effective in removing hydrogen from steel than is exposure to dry air at the same temperature, and immersion in hot water is even more effective. Of course, all three methods are considerably more effective than storage in air at room temperature. One investigation showed that recovery of ductility was more rapid at 212 F for specimens stored in water or 3 percent NaOH solution than for those stored in oil or dry argon. Surprising as it may seem, hydrogen is readily removed from steel in a dry-hydrogen atmosphere. This is possible because hydrogen atoms can diffuse against a high pressure of molecular hydrogen, if the partial pressure of dissociated hydrogen is low, as it is at near-ambient temperatures and ordinary pressures. The marked effect of environmental conditions on the rate of hydrogen removal from steel is well demonstrated by a comparison of the rates from steel immersed in water and steel held in a vacuum, both at 100 F, as shown in Figure 14. The time to remove 50 percent of the hydrogen from the steel investigated was only 1 hour for specimens immersed in water and 5.8 hours for specimens held in a vacuum at the same temperature. The fact that such large differences in hydrogen-removal rate do exist shows that surface reactions (rather than diffusion) can be rate determining.

The presence of a more-or-less impermeable metal coating, such as cadmium, makes the evolution of hydrogen from the interior of the base steel more difficult; this behavior may serve to aggravate the effects of embrittlement and delayed failure of electroplated steel. An appropriate baking treatment (23 hours at 375 to 400 F is used for many cadmium-plated steel parts) may restore most or all of the ductility to the plated high-strength steel. However, frequently such a treatment does not overcome the tendency for hydrogen-stress cracking to occur. Delayed failures have occurred after electroplated parts have been baked for times at least as long as 100 hours. Sometimes the static loading test may indicate essentially no recovery as a result of a baking treatment. It has been shown conclusively that data obtained in a short-time tensile test are not suitable criteria of the susceptibility to hydrogen-stress cracking. Furthermore, baking does not insure elimination of the susceptibility to such failures. Figure 15 shows how a chromium electroplate acted as a barrier to hinder evolution of hydrogen on aging at room temperature and, hence, to hinder recovery of ductility. Figure 16, which shows recovery by baking at 375 F, demonstrates how chromium plate also hinders recovery of ductility during a baking treatment. This figure also shows that the cadmium plate commonly used for corrosion protection of high-strength steel parts acts as an even more effective barrier. Such other coatings as zinc, tin, gold,

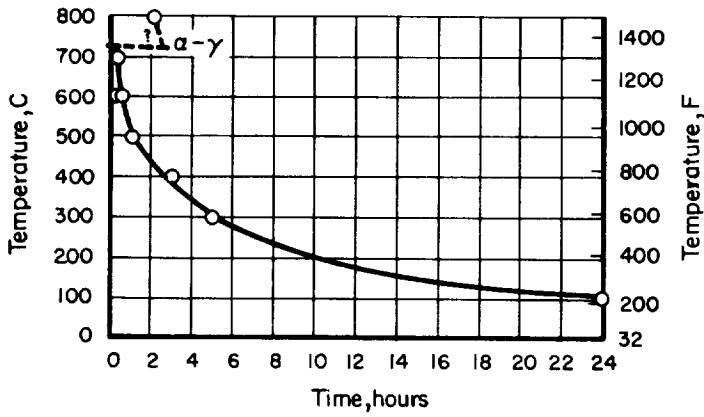


FIGURE 10. RELATION OF TEMPERATURE TO ANNEALING TIME NECESSARY FOR REMOVING HYDROGEN EMBRITTLEMENT FROM MILD-STEEL SPECIMENS⁽¹⁷⁾

Tensile specimens 0.505 inch in diameter.

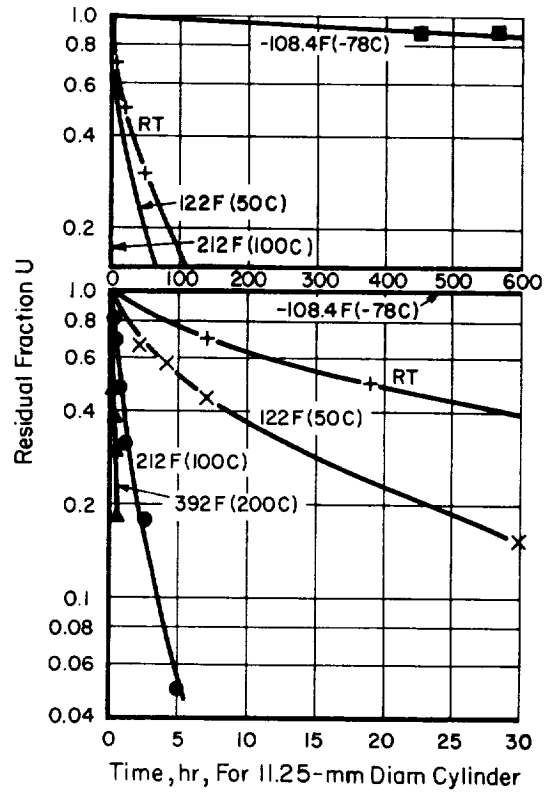


FIGURE 11. EFFECT OF TEMPERATURE ON RATE OF HYDROGEN EVOLUTION FROM 2.5Ni-Cr-Mo STEEL⁽¹⁶⁾

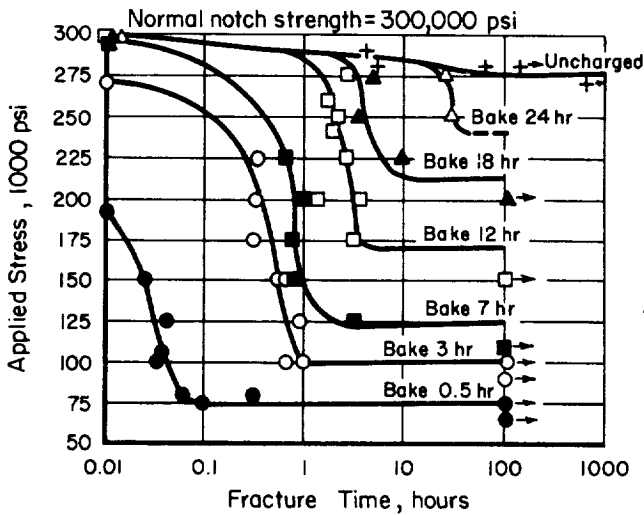


FIGURE 12. STATIC-FATIGUE CURVES FOR VARIOUS HYDROGEN CONCENTRATIONS CORRESPONDING TO DIFFERENT BAKING TIMES AT 300 F AFTER CATHODIC CHARGING⁽¹⁸⁾

Sharp-notch specimens; 230,000-psi strength level.

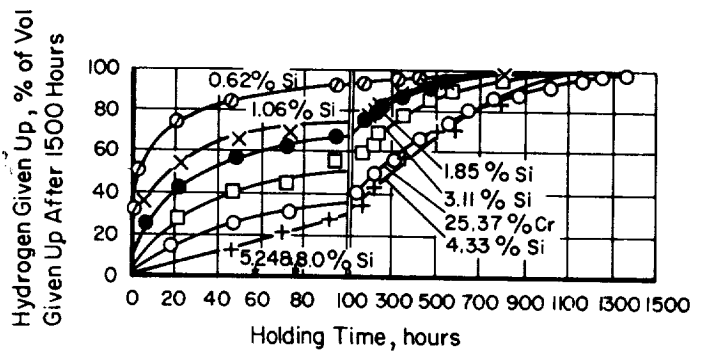


FIGURE 13. INFLUENCE OF SILICON AND CHROMIUM IN FERRITE ON EFFUSION OF HYDROGEN AT ROOM TEMPERATURE⁽¹⁵⁾

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tungsten, thin oxide films, and a high-temperature glass enamel reportedly retard permeation of hydrogen through steel, but a coating of lacquer has little effect.

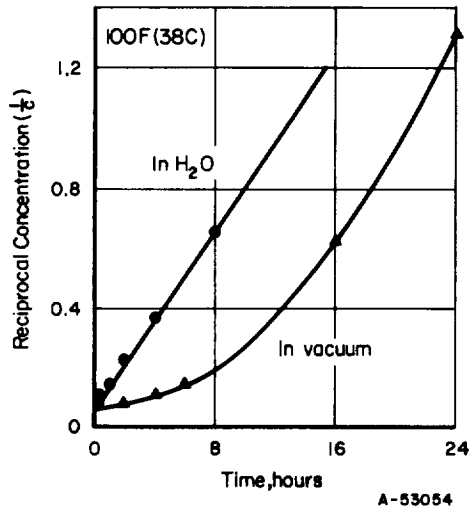


FIGURE 14. PLOT SHOWING THAT THE REMOVAL OF HYDROGEN FROM STEEL IN WATER AND IN A VACUUM OBEYS DIFFERENT RATE LAWS⁽¹⁹⁾

(The difference between initial slopes is significant; c = concentration of hydrogen in steel.)

The recovery of the original properties of high-strength steel parts that have been cadmium plated is an important problem in the aircraft industry. Much effort has gone into the development of plating baths that are more efficient and, therefore, plate out less hydrogen at the steel surface. Variations in the structure of the cadmium plate have a marked influence on the effectiveness of a baking treatment. A somewhat porous plate offers less resistance to the effusion of hydrogen. Methods have been developed to intentionally produce a porous cadmium electroplate which permits hydrogen to diffuse out in a subsequent baking treatment while still providing what appears to be reasonable corrosion resistance. One investigation showed that the addition of very small amounts of a brightener to a cadmium-plating bath greatly reduced the recovery from hydrogen embrittlement, because the plate was more dense.

Strength Level and Applied Stress

Both the minimum stress and the time required to produce delayed brittle failure by hydrogen decrease as the nominal tensile strength of the steel is increased. Thus, hydrogen-stress cracking is an increasingly severe problem as the strength level of the steel is increased.

Hydrogen-induced delayed brittle failures may occur over a wide range of applied tensile stress, and the time for failure is not affected greatly by variations in the applied stress. Also, for given specimens, charging conditions, and test procedures, there is a minimum critical value of applied stress (frequently called the lower critical stress) below which failure does not occur in a given material for an indefinite period of time. The lower critical stress is important because, for a given hydrogen concentration and strength level (and a given notch sharpness in the case of notched specimens), it is the lowest applied stress sufficient to initiate a crack. In other words, the lower critical stress is a threshold stress, above which failure is inevitable (given a long enough time under stress) and below which the steel is undamaged.

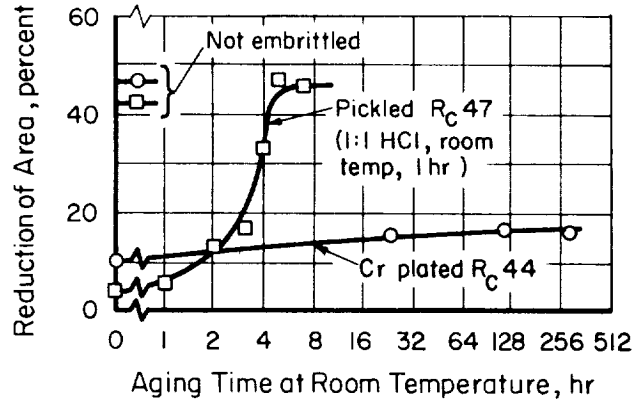


FIGURE 15. EFFECT OF AGING ON THE HYDROGEN EMBRITTLEMENT OF PICKLED AND CHROMIUM-PLATED TENSION SPECIMENS OF 4340 STEEL (0.505-IN. DIAM.) (DATA BY NORTH AMERICAN AVIATION)⁽²⁰⁾

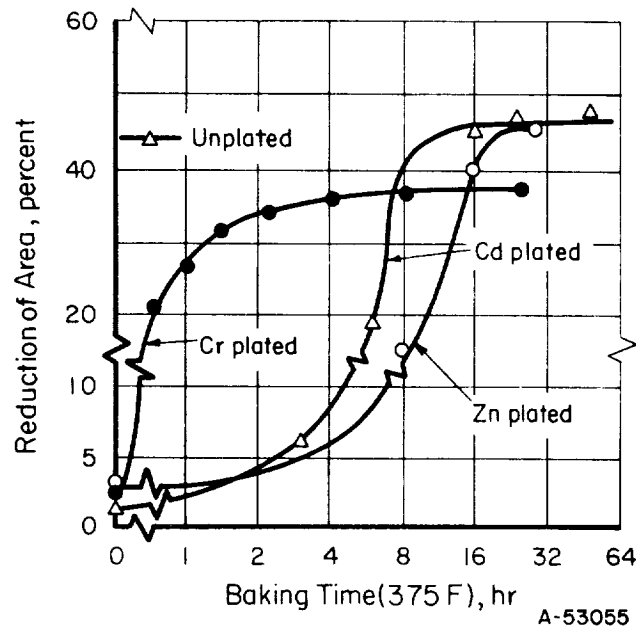


FIGURE 16. EFFECT OF BAKING TIME ON HYDROGEN EMBRITTLEMENT OF CHROMIUM-, CADMIUM-, AND ZINC-PLATED SPECIMENS (DATA BY NORTH AMERICAN AVIATION)⁽²⁰⁾

4340 Steel, Hardness = Rockwell C 45.

The results of tests of hydrogen-charged material under static load usually are plotted as sustained load versus time to failure. Such a plot is shown in Figure 1 for the case of notched specimens precharged with hydrogen. The effects of both strength level and applied stress on the time for delayed failure are shown. Relatively low applied stresses were sufficient to produce hydrogen-stress cracking. An applied stress as low as 40 percent of the yield strength (for a steel of 270,000-psi ultimate tensile strength) caused failure in only a few hours under sustained load. For a given strength level, there appeared to be only a slight dependence of failure time on the applied stress. For this type of experiment in which precharged, notched specimens were used, the time to failure was of the same order of magnitude, regardless of the strength level. The plateau of the delayed-failure curves at high applied stress (that is, the upper plateau) coincided with the notched tensile strength for a given strength level.

Other experiments have been performed in which smooth (unnotched) specimens were continuously charged with hydrogen cathodically while under sustained load. The results of one such investigation are shown in Figure 17. As the strength level was decreased from 300,000 psi to 142,000 psi for the tempered-martensite structure, the time to rupture in the higher range of applied stress increased by a factor of approximately 100. Also, the applied stress required to cause rupture in 10,000 minutes increased from 15,000 to 45,000 psi as the strength level was decreased in that range. These results were obtained under severe cathodic charging conditions. Although it is unlikely that the specific conditions of these tests would be encountered in service, the results obtained show that hydrogen entering the steel while it is under stress can cause it to lose up to 95 percent of its ability to withstand a sustained load, in the case of steel heat treated to a high strength level (300,000-psi steel failed at 15,000 psi). Even at the lowest strength level tested for the tempered martensite (142,000 psi), the steel lost approximately two-thirds of its load-carrying ability. In these experiments, rupture occurred in a tempered-martensite structure having a tensile strength as low as 142,000 psi and in pearlitic material with a tensile strength of only 100,000 psi. However, service failures nearly always have been restricted to steels having a higher strength level. This can be attributed to the fact that in the laboratory experiments the specimens contained more hydrogen than would be expected in service.

REVIEW OF CURRENT LITERATURE AND INDUSTRIAL PRACTICES

Pickling and Cleaning Processes as a Source of Hydrogen Embrittlement

During processing and fabrication, metals and alloys acquire scale or oxide coatings as well as other surface contamination, and various cleaning processes are employed to remove these surface contaminants. The commonly employed cleaning processes include abrasive cleaning (such as grit blasting and tumbling), salt-bath descaling, alkaline descaling, and acid pickling for the removal of surface oxides; and alkaline cleaning, emulsion cleaning, solvent cleaning, and vapor degreasing for the removal of oil, grease, and dirt. Some of these cleaning processes may be performed cathodically or anodically.

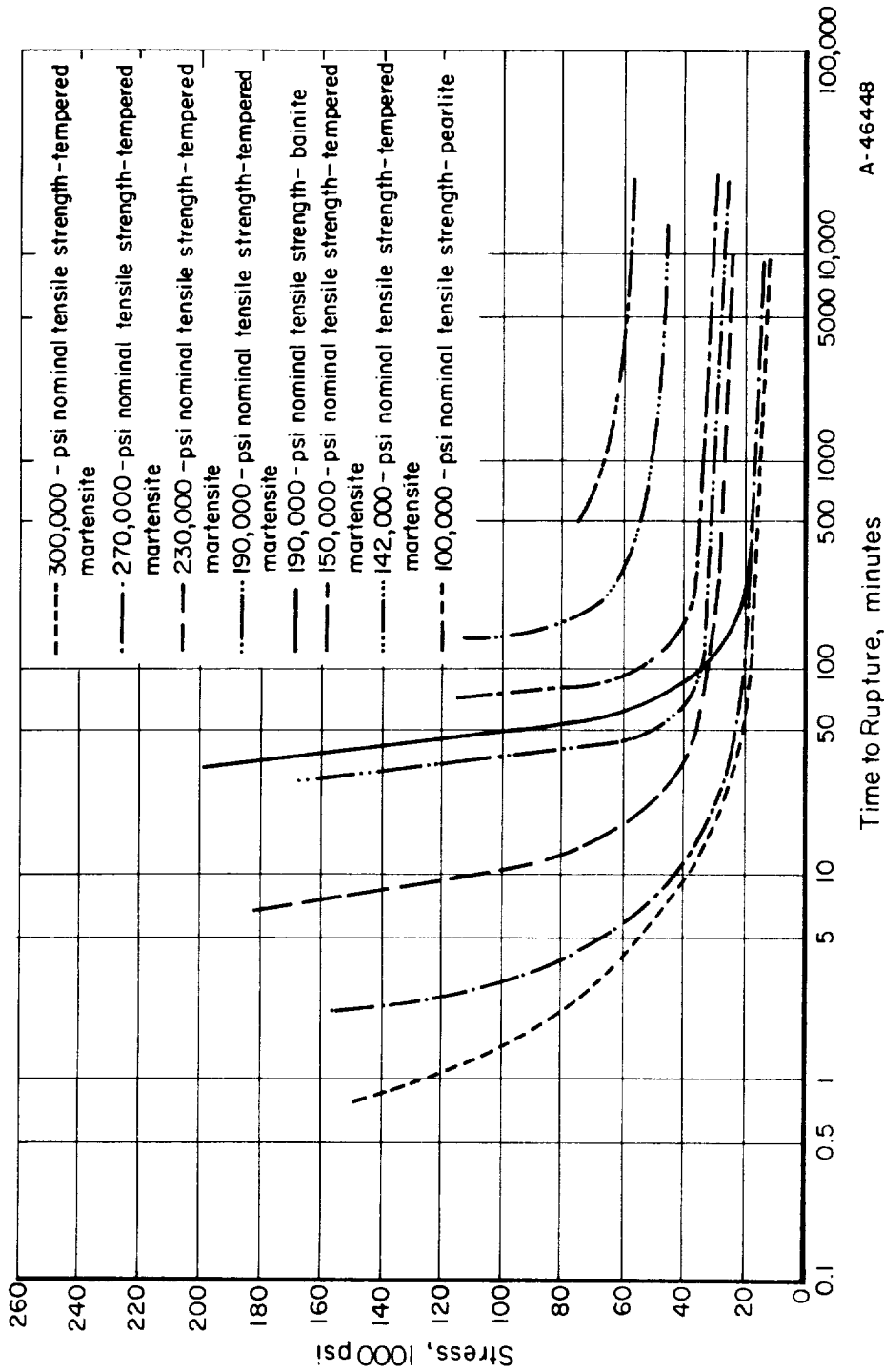


FIGURE 17. DELAYED-FAILURE CHARACTERISTICS OF UNNOTCHED SPECIMENS OF AN SAE 4340 STEEL DURING CATHODIC CHARGING WITH HYDROGEN UNDER STANDARDIZED CONDITIONS(21)

Battelle Charging Condition A:

- Electrolyte: 4 percent by weight of H_2SO_4 in water
- Poison: 5 drops per liter of cathodic poison composed of 2 g phosphorus dissolved in 40 ml CS_2
- Current density: 8 ma/in.²

Selection of the cleaning process is influenced mainly by the type of surface contamination to be removed, the required degree of cleanliness, and the cost.

Of these cleaning processes, acid pickling, acid cleaning, and cathodic cleaning embrittle high-strength steels, and vapor blasting may result in embrittlement. The difference between acid pickling and acid cleaning is a matter of degree, and there is often some overlapping in the usage of these terms. In general, acid pickling refers to a more severe treatment for the removal of scale from semifinished mill products, forgings, or castings, whereas acid cleaning is the term most frequently used when the acid solution is employed for final or near-final preparation of metal surfaces prior to electroplating, painting, or storage. (22) In this report all acid pickling and cleaning processes will be referred to as acid pickling.

Acid pickling is used to:

- (1) Completely remove the scale by the acid treatment alone, or after the scale has been conditioned in a caustic bath
- (2) Remove contaminated or damaged surface metal
- (3) Remove oxide film
- (4) Activate the metal surface for plating by removal of invisible oxide or passivating films
- (5) Passivate the metal or alloy to provide greater corrosion resistance.

Pickling in hot concentrated solutions of sulfuric or hydrochloric acid is declining in use as a single treatment for complete scale removal from mill products and fabricated parts; with increasing frequency, pickling, at acid concentrations of about 3 percent and at temperatures of 140 F or lower, is being used as a supplementary treatment following abrasive blasting or salt-bath descaling. (22)

Sulfuric acid and hydrochloric acid solutions are commonly used to pickle carbon and low-alloy steels. Nitric acid is used in pickling stainless steels and occasionally is employed to oxidize scale surfaces to facilitate pickling. Hydrofluoric acid is sometimes added to the bath to accelerate pickling. The acid-pickling solutions for the high-strength, high-temperature alloys are usually mixtures of nitric and hydrofluoric acids. Sometimes a scale-conditioning treatment in a molten-caustic bath is required before the scale can be removed satisfactorily by pickling. The scale-conditioning treatments often remove most of the scale, but usually leave a small amount which must be removed by pickling. The descaling rates of the molten-salt baths are generally more rapid than those for acid pickling. However, because the salt baths generally contain no hydrogen and they attack the scale and not the underlying metal, danger of hydrogen embrittlement of high-strength steel is eliminated. Also the supplementary acid pickling is accomplished with more dilute solutions, lower temperatures, and shorter times than are used in conventional pickling. These factors minimize metal loss and the danger of hydrogen embrittlement.

Alkaline descaling or alkaline derusting is used to remove rust, light scale, and carbon smut from carbon, alloy, and stainless steels, and heat-resisting alloys. A number of proprietary compounds are available; they are composed primarily of sodium hydroxide (60 percent or more) but also contain chelating agents.

Alkaline descaling is more costly and slower in its action than is acid pickling, but there is no loss of metal by the alkaline method because chemical action stops when the rust or scale is removed. Alkaline descalers are used mainly for applications where risk of hydrogen embrittlement, loss of metal, or etched surfaces cannot be tolerated.

Part of the action in the pickling of steel consists of undermining the scale by the attack of the metal with the acid. Because iron is electrochemically less noble than hydrogen, it replaces hydrogen from solutions of its ions (acids). When a piece of iron or steel is placed in a solution of a nonoxidizing acid with which it reacts, as in pickling, local anodes and cathodes are established and atomic hydrogen is released at the local cathodes on the steel surfaces. A portion of this atomic hydrogen enters the steel, and the remainder combines to form molecular hydrogen which is insoluble in steels. The important factor here is the amount of hydrogen which enters the metal and not the total amount of hydrogen evolved at the metal surface. The fraction of the hydrogen atoms that recombine and thus do not enter the steel, and the rate of steel dissolution are greatly affected by inhibitors and promoters (cathodic poisons) in the solution.

Promoters generally build up in the bath as a result of the pickling process and may lead to a considerable increase in hydrogen entry. Severe damage may be caused by an accumulation of hydrogen sulfide, arsenic, antimony, and sulfur in the pickling bath. (23)

Cathodic pickling of iron and steel is employed to overcome some of the difficulties encountered in ordinary (nonelectrolytic) acid pickling. Although cathodic pickling is more expensive than acid pickling, it can remove tightly adhering scales much faster because of the greater evolution of hydrogen which agitates the pickling solution, reduces the scale, and tends to loosen the scale from the steel surface. This method reduces the loss of valuable metal, minimizes surface roughening, and reduces the consumption of acid. However, problems related to the absorption of atomic hydrogen by the steel are likely to become more severe when pickling is performed cathodically. Blistering and cracking become even more severe if arsenic or selenium, which are common impurities in acids, are present during cathodic pickling. However, by adding a trace of tin salt to the acid, it is possible to realize the advantages of cathodic pickling while minimizing the disadvantages. A very thin layer of metallic tin is deposited on any portion of the metal which becomes bare of scale. This layer hinders the evolution of hydrogen because of the high overvoltage of tin, and it also imposes a barrier to retard the entry of atomic hydrogen into the steel.

One way to reduce the evolution of hydrogen resulting from attack of the metal is to make the steel the anode during acid pickling (anodic pickling). This process should effectively prevent the evolution of hydrogen on the steel and, therefore, its entry into steel. However, anodic pickling sometimes increases both the attack on the metal and surface roughening, and it may increase acid consumption. Therefore, this process is used most frequently for material from which the scale previously has been removed mechanically, the object being to produce a surface suitable for electropolishing.

Although many papers have been written on the subject of acid pickling of steel, only limited information has been published on the relationship between the rate at which steel is dissolved and the rate of hydrogen absorption by steel as a function of acid type and acid concentration. Bablik⁽²⁴⁾ pointed out that the rate of dissolution of iron and steel is a function not only of acid type, acid concentration, and temperature

but, also, of the composition of the workpiece (particularly in regard to levels of carbon, phosphorus, copper, and sulphur) and the processing history of the material (particularly the degree of cold work).

Zapffe and Haslem,⁽²⁵⁾ using constant-rate, single-bend tests, observed that carbon steels and stainless steels were not embrittled by immersion in nitric acid. The low level of hydrogen introduced into steel during nitric-acid pickling was recognized by Darken and Smith⁽²⁶⁾ who employed a 1-minute etch at room temperature in 25 volume percent nitric acid to prepare specimens for use in their studies of hydrogen behavior in steel.

The unique behavior of nitric acid with respect to hydrogen embrittlement is related to its oxidizing characteristics. It has long been recognized that metals react with the acid by replacing hydrogen to form the corresponding nitrates and that the hydrogen evolved during this process is immediately consumed with the formation of compounds containing nitrogen of lower valency. Therefore, nitric acid has been regarded as causing no hydrogenation. However, Balezin and Nikol'skii^(27,28) and Hudson, Norris, and Stragand⁽¹⁹⁾ reported that under some circumstances nitric acid solutions can cause embrittlement of steel. Balezin and Nikol'skii found that steels that contained 0.17, 0.6, 0.9, and 1.1 percent carbon, respectively, did not absorb hydrogen when pickled in 1.5 and 2N nitric acid solutions, but did absorb hydrogen in 0.5N nitric acid solution. The range of nitric acid concentration which produced the most severe embrittlement in wire at 64 F was from 0.3 to 0.8N. They attributed this embrittlement in the dilute solution to the likelihood that not all of the hydrogen evolved was oxidized.

The reason that oxidizing acids are not employed more widely as a simple means of avoiding hydrogen troubles without resorting to an external potential is that practically every oxidizing acid or acidic mixture introduces some new objection. Nitric acid, for example, is unpleasant because of the fumes evolved and its action on the skin.

Recently, Hudson⁽²⁹⁾ studied the hydrogen absorption rate and dissolution rate of a low-carbon steel in sulfuric, hydrochloric, phosphoric, and nitric acids. He found that the dissolution rate of steel in 2N and 10N solutions of nitric acid at 100 F was much faster than for the same concentrations of the other acids studied, although the dissolution rate for 0.05N and 0.5N nitric acid was not significantly different than that for sulfuric acid at these concentrations. Dissolution in sulfuric acid solutions at concentrations of 0.5N and 2N at 100 F was more rapid than dissolution in hydrochloric acid of the same concentration, but for 10N acid the rate in hydrochloric acid was greater than for sulfuric acid. Dissolution rates in phosphoric acid solutions at 100 F were slower over the entire concentration range than for the other acids at comparable concentrations. These data are presented in Figure 18. The dissolution rates in 2N acid solutions increased with an increase in temperature (Figure 19). The amount of hydrogen introduced into steel during dissolution in nitric acid solutions was much lower than for the other acids, as is shown in Figure 20. Generally the hydrogen concentration increased linearly with the square root of the immersion time. An increase in temperature did not increase the amount of hydrogen absorbed from a 2N HNO₃ solution; however, the amount of hydrogen absorbed from the 2N solutions of other acids by the low-carbon steel did increase with increasing temperature (Figure 21). Although the dissolution rates at 100 F differed among sulfuric acid, hydrochloric acid, and phosphoric acid solutions at the various concentration levels, the percentage of theoretically available hydrogen absorbed by the steel after a given weight loss of metal

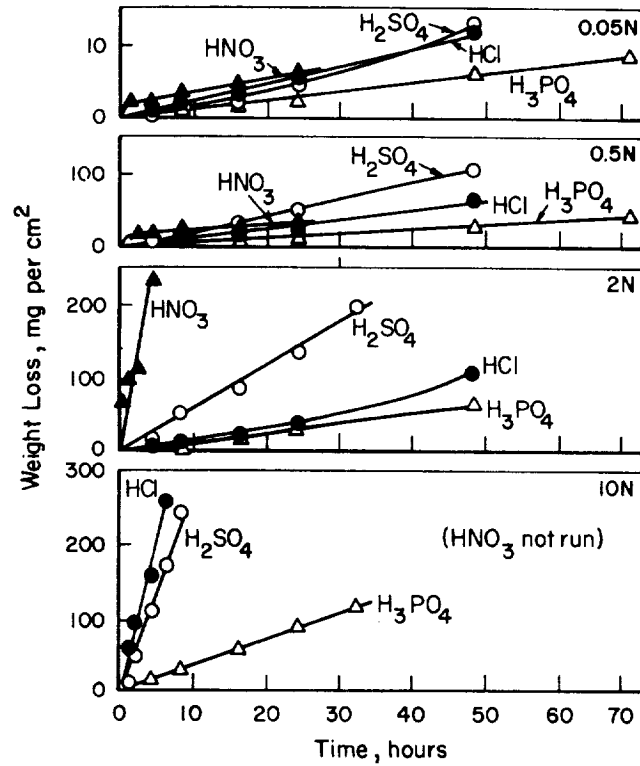


FIGURE 18. COMPARISON OF DISSOLUTION RATES FOR LOW-CARBON STEEL AT 100 F AS A FUNCTION OF ACID AND CONCENTRATION⁽²⁹⁾

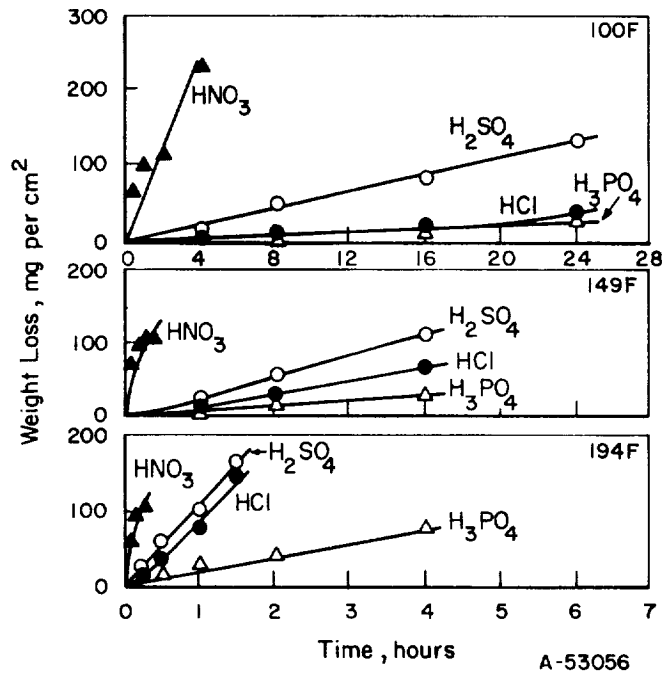


FIGURE 19. DISSOLUTION RATE OF LOW-CARBON STEEL IN 2N ACIDS AS A FUNCTION OF TEMPERATURE⁽²⁹⁾

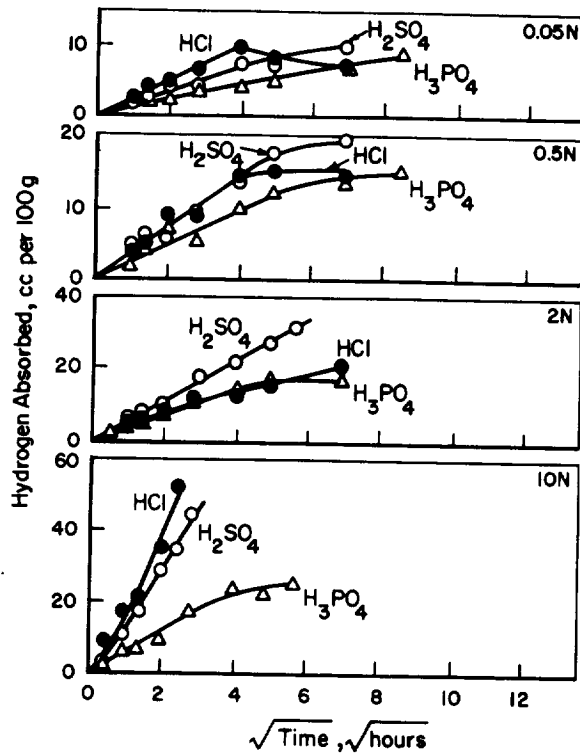


FIGURE 20. HYDROGEN ABSORPTION BY LOW-CARBON STEEL AT 100 F IN SOLUTIONS OF SULFURIC, HYDROCHLORIC AND PHOSPHORIC ACIDS⁽²⁹⁾

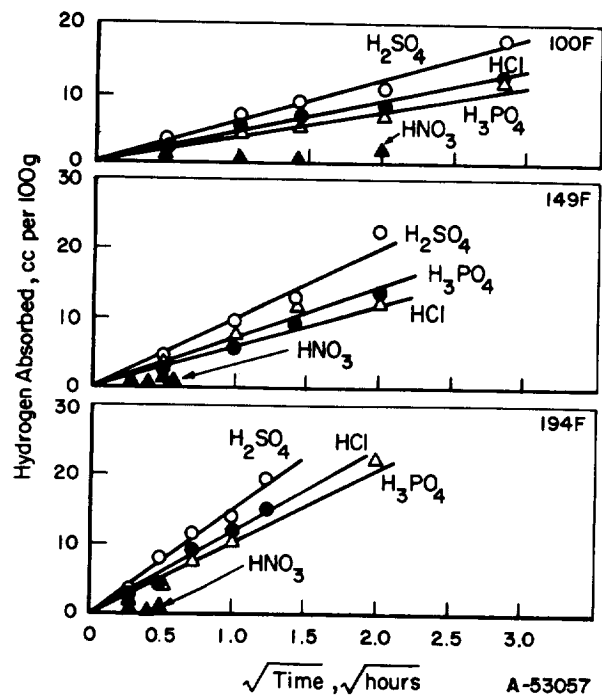


FIGURE 21. HYDROGEN ABSORBED BY LOW-CARBON STEEL DURING IMMERSION IN 2N ACIDS AS A FUNCTION OF TIME AND TEMPERATURE⁽²⁹⁾

did not vary significantly among these three acids. For each acid, particularly when the weight loss was low, the percentage of available hydrogen absorbed for a given metal weight loss decreased with increasing temperature.

Sachs and Odgers⁽³⁰⁾ studied the amount of hydrogen absorbed and its effect on the ductility of pure iron and mild-steel screw wire after pickling or cathodic charging. The pickling solution was 50 percent HCl at room temperature and the cathodic charging conditions were 10 percent KOH electrolyte at a current density of 0.1 amp/in.². These investigators found that pure iron absorbed very little hydrogen as a result of pickling in 50 percent HCl. In the mild steel, the hydrogen content increased with pickling time; the total hydrogen occlusion was greatly influenced by carbon content but very little by grain size. In the ferrite matrix, absorption was probably diffusion controlled. Cold work significantly increased both the rate of hydrogen absorption and the total amount absorbed and smoothed out the effect of carbon segregation. They concluded that hydrogen absorption during pickling was profoundly affected by the presence of inclusions in pure iron and in mild steel, but electrocharging revealed the characteristic hydrogen absorption behavior of the matrix. The hydrogen absorbed by pure iron did not cause enough embrittlement for the loss of ductility to be detected in the constant-rate bend test. In mild steel, hydrogen embrittlement was observed, but there was no direct correlation between loss of ductility and hydrogen content, which again suggests that embrittlement depends more on the hydrogen distribution than on the total hydrogen content of a specimen. Embrittlement was detected at shorter pickling times and was most severe in lightly drawn mild steel, but in all cases the ductility was at its minimum long before the saturation concentration of hydrogen was attained, as is shown in Figure 22.

Probert and Rollinson⁽³¹⁾ studied the embrittlement of high-strength steels during chemical and electrochemical processing using a constant-rate bend test and found that acid pickling and cathodic treatment in NaOH/NaCN solution severely embrittled high-strength steels, as shown in Figures 23 and 24. They also showed that the degree of embrittlement was dependent on the carbon content and strength level of the steel, with the severity increasing with increasing carbon content and increasing strength level. While investigating the embrittling characteristics of sulfuric-acid electrolytic etching solutions, these investigators found that the bend angle required to produce fracture could be varied by simply altering the cathodic/anodic etching times. Further work confirmed that this effect was due to the partial removal of the hydrogen-contaminated layer, and the discovery led to development of a technique for establishing the depth of hydrogen penetration. Generally, it was found that, by removal of 3 mils of metal per surface by controlled anodic etching, it was possible to restore the angle of bend at fracture of embrittled (electrolytically etched) material to a value slightly above the value for unetched material.

Gurklis, et al,⁽³²⁾ showed that short acid dips prior to cadmium plating of SAE 1095 spring steel (tensile strength of 233,000 psi) significantly reduced its tensile ductility. For pieces pickled 1 minute in 10 percent hydrochloric acid, the reduction in area was reduced by one-half. However, the specimens were not susceptible to delayed failure under the conditions of their test. Similarly, a 10-minute cathodic pickle in sulfuric acid at a current density of 10 amps/ft.² (asf) did not produce delayed brittle failures at stresses up to 195,000 psi. However, after a 20-hour cathodic pickle at 30 asf, the specimens consistently exhibited delayed failures at stresses above about 117,000 psi. A vigorous pickling treatment was also required to obtain delayed fracture of spring steel bent almost to the breaking point in compression between the jaws of a vise.

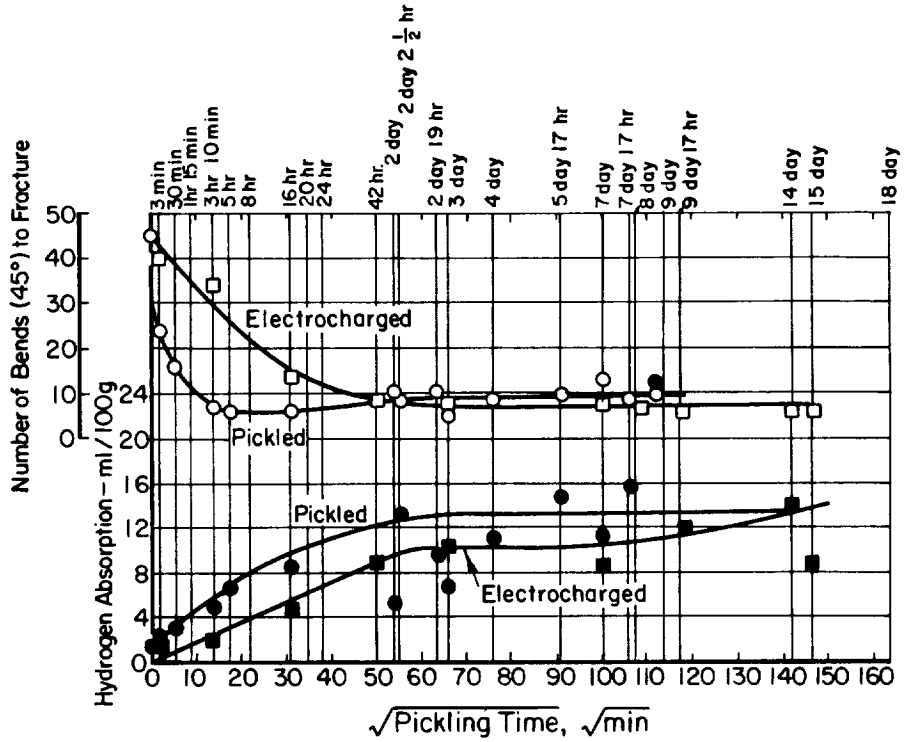


FIGURE 22. EFFECT OF PICKLING AND ELECTROCHARGING ON "AS RECEIVED" MILD STEEL SCREW WIRE THAT HAD BEEN COLD REDUCED 10 PERCENT IN A SIZING DRAW⁽³⁰⁾

Surface cleaned with emery paper.

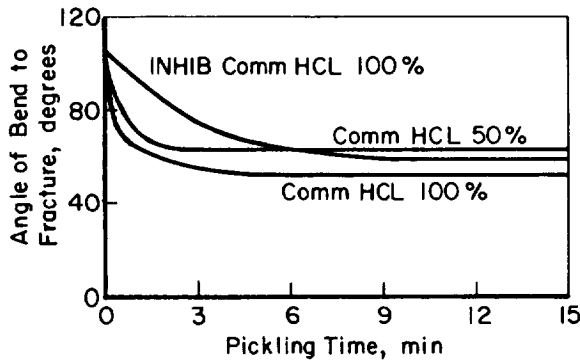


FIGURE 23. HYDROGEN EMBRITTLEMENT OF GAUGE STEEL BY PICKLING IN ACID SOLUTION⁽³¹⁾

Tool steel for feeler gages (1.0-1.8 percent C),
550 Bhn.

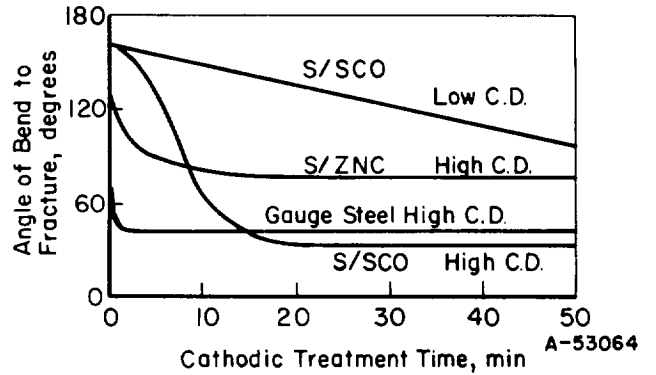


FIGURE 24. HYDROGEN EMBRITTLEMENT PRODUCED BY CATHODIC TREATMENT IN NaOH/NaCN SOLUTION AT LOW AND HIGH CURRENT DENSITIES⁽³¹⁾

	Hardness, Bhn
Rolls-Royce Gauge Steel = Tool steel for feeler gages containing 1.0-1.8 percent C	558
Rolls-Royce S/SCO = Specification FV 535	367
Rolls-Royce S/ZNC = British Std. S. 82	410
Composition of British Std. 2S. 82	
C 0.12-0.18	Mo 0.15-0.35
Cr 1.0-1.4	Ni 4.0-4.5

A method frequently used to reduce the problems related to both metal attack and hydrogen liberation is to add inhibitors to the pickling bath. Inhibitors minimize metal loss, reduce the extent of hydrogen embrittlement, protect the metal against pitting (caused by overpickling) and reduction in surface quality, reduce acid fumes resulting from excessive reaction between the acid and basis metal, and reduce acid consumption.

Both natural and synthetic organic compounds are used as inhibitors. Natural compounds include low-grade bran flour, gelatin, glue, sludge from petroleum, animal wastes, sulfonated coal-tar products, asphaltum, and wood tars. The synthetic inhibitors commonly used today are organic substances that contain nitrogen and sulfur, such as pyridines, quinidines, aldehydes, and thioaldehydes. The accumulation of iron sulfates in the acid solution also inhibits the activity of the acid but reduces the effectiveness of the solution for cleaning and brightening the steel.

Inhibitors are commonly used in ordinary acid-pickling baths without an applied potential or current. However, a combination of inhibitor and cathodic current can be a very economical procedure. With this arrangement, the current required is much lower than in the absence of an inhibitor, and the inhibitor concentration required is far below that needed in the absence of an external applied current. It is claimed that the combination avoids the chief difficulties encountered with each method, that is, the problem of hydrogen embrittlement and delayed cracking associated with cathodic pickling at high current densities, and the loss of time associated with the use of inhibitors, some of which appreciably retard the removal of scale. The current density can be reduced to 1/100 of that needed when no inhibitor is used, and the inhibitor concentration can be reduced to 1/10 of that needed when no current is employed. (33)

Evans, (34) in describing the use of inhibitors, pointed out that if the only objective in using an inhibitor is to reduce the metal loss and the consumption of acid, any substance that obstructs any one of the essential steps of the corrosion process can be used. However, in practice an inhibitor must meet other requirements. Reducing the total corrosion, that is, the total amount of hydrogen produced, does not suffice. It is particularly necessary to reduce that fraction of the hydrogen which enters the metal and causes either blistering or cracking.

Zapffe and Haslem⁽³⁵⁾ studied the effect of 15 commercial inhibitors on hydrogen embrittlement and found that the chemical composition of the steel was the deciding factor in determining the efficiency of the inhibitor. Practically all the commercial inhibitors failed completely when pickling stainless steel. In fact, 11 of them actually increased hydrogen embrittlement. On a mild steel (0.18 percent C) the results were somewhat better. Of the 15 inhibitors investigated, 7 failed completely, 4 prevented hydrogen embrittlement when used in quantities which greatly exceeded the usually recommended concentration, and the 4 remaining inhibitors proved effective when used in prescribed quantities.

Meyer⁽²³⁾ investigated the effects of 17 proprietary inhibitors on hydrogen embrittlement using a patented steel wire containing 0.58 percent carbon. He found that only one inhibitor gave substantial protection, but all gave some protection. In a 15 percent H₂SO₄ solution, the protective values* ranged from 5 to 87.5 percent, while corresponding values for pickling acid that contained 7.5 percent (by weight) H₂SO₄ as well as 2.3 lb/gal of FeSO₄ varied between 8.5 and 94 percent. These protective values were based on the number of stress reversals applied to the wire specimens to

$$*\text{Protective value (percent)} = \frac{Br - Bg}{Br} ,$$

where Br = loss of stress reversals in unmodified acid; Bg = loss of stress reversals in the inhibited acid.

produce fracture. The results of this investigation also showed that the inhibiting action of the pickling additive on metal corrosion is in no way related to its inhibiting action on hydrogen embrittlement.

Anderson and associates⁽³⁶⁾ studied the effect of certain organic inhibitors on the absorption of hydrogen by AISI 1095 steel pickled in hydrochloric acid. Their work showed the importance of the reaction between the hydrogen and the inhibitor in preventing the hydrogen from entering the steel, and thus preventing embrittlement.

Several studies have been conducted to evaluate the effectiveness of acetylenic alcohols and derivatives for limiting both hydrogen absorption by steel and dissolution of steel during pickling. Although information on the degree of protection of mild steel by acetylenic acid inhibitors is presented in several papers, quantitative information is not given on the hydrogen absorption by steel immersed in acid solutions containing these inhibitors. Hudson and Riedy⁽³⁷⁾ studied the effectiveness of 16 water-soluble acetylenic compounds and two commercial inhibitors used in 2N sulfuric acid at 100 F. Ten acetylenic alcohols and 6 acetylenic diols were studied. The effectiveness of these compounds was determined by measuring the metal loss and the amount of hydrogen absorbed (warm-extraction method) for a low-carbon steel immersed in these solutions for either 4 or 24 hours. Six of the acetylenic alcohols and two of the acetylenic diols were similar in effectiveness to the two commercial proprietary inhibitors examined in their ability to retard the dissolution of steel in acid. Most of the acetylenic compounds were as good as, or better than, the better of the two commercial proprietary inhibitors in limiting hydrogen absorption by the steel. Most of the acetylenic inhibitors that were effective at 100 F also were effective at 180 F. The commercial inhibitors, however, were not nearly so effective in limiting hydrogen absorption at the higher temperature as they were at 100 F (Table 4). References 38 and 39 present data relative to the effects of various inhibitors in reducing the corrosion rate of certain materials during acid pickling in hydrochloric acid. Every and Riggs⁽³⁹⁾ showed that mixtures of organic inhibitors that contained both a nitrogen and a sulfur derivative were generally more effective than one or both of the parent compounds and that these mixtures have excellent inhibitory characteristics at low concentrations. The data also verify the findings of other investigators that the protective value of sulfur-containing compounds is in general superior to that of nitrogen-containing materials.

The mechanism by which organic inhibitors reduce attack and limit hydrogen absorption is still not definitely known. It is believed that the polar atoms of nitrogen and sulfur serve to attach the molecules to the metal surface at points where otherwise some essential step in the corrosion process would occur. Generally, the efficiency of inhibitors increases as the length and number of side chains attached to the polar atom increase. However, some small molecules, such as formaldehyde, can act as inhibitors. Most of the present effective inhibitors interfere mainly with the anodic reaction, although the cathodic reaction also is usually retarded somewhat.

Although certain inhibitors have been shown to be effective in reducing the absorption of hydrogen by steel during acid pickling, it is best to avoid pickling and all cathodic cleaning processes altogether for high-strength steels, which are especially susceptible to hydrogen-stress cracking. For these materials, scale is best removed mechanically, and only alkaline or anodic cleaning processes should be used.

TABLE 4. EFFECTIVENESS OF PICKLING INHIBITORS IN 2N SULFURIC ACID CONTRASTED AT 100 AND AT 180 F FOR 4-HOUR IMMERSION TIME⁽³⁷⁾

Inhibitor	Inhibitor Concentration	Weight Loss, mg/cm ²		Percent Inhibition		Hydrogen Absorbed, cc/100 g		% Limitation of Hydrogen Absorption	
		100 F	180 F	100 F	180 F	100 F	180 F	100 F	180 F
1-Propyn-3-ol	0.05M	0.4	11.7	98	95	1.0	3.1	88	86
1-Pentyn-3-ol	0.05M	0.2	2.3	99	99	1.0	1.2	88	95
1-Hexyn-3-ol	0.05M	0.2	3.2	99	99	1.2	0.3	85	99
4-Methyl-1-pentyn-3-ol	0.05M	0.2	4.9	99	98	0.9	0.5	89	98
1-Ethynylcyclohexan-1-ol	0.05M	0.4	1.9	98	99	0.7	0.3	92	99.9
2-Butyn-1,4-diol	0.05M	0.4	7.0	98	97	1.4	3.1	83	86
3,6-Dimethyl-4-octyn-3,6-diol	0.05M	0.6	164.4	97	24	0.9	19.5	89	12
3-Methyl-1-pentyn-3-ol	0.05M	0.4	114.7	98	47	0.7	16.1	92	27
Inhibitor A	0.25 volume percent	0.2	0.3	99	99.9	1.3	5.6	84	75
Inhibitor B	0.25 volume percent	0.2	1.4	99	99.4	2.4	14.6	71	34
Uninhibited acid	--	21.1	216.5	0	0	8.3	22.1	0	0

Electroplating as a Source of Hydrogen Embrittlement

Electroplating of metallic materials is done for a variety of reasons which include ornamentation, protection against corrosion, building up of worn parts, improving wear resistance, improving light reflectance, or otherwise changing the physical and chemical properties of the surfaces being plated. The most common reason for electroplating high-strength steel parts used in the aircraft and aerospace industries is for protection against corrosion. However, the application of electrodeposited coatings to solve corrosion problems can make the part susceptible to failure by another mechanism, namely, hydrogen-stress cracking.

Steel has been found to be embrittled by virtually all of the common electroplating processes, including cadmium, chromium, zinc, tin, nickel, lead, copper, and silver. Early studies of this problem showed that generally the degree of embrittlement becomes more severe as the hardness level (strength) of the steel is increased. These early studies also showed that hydrogen entry into specimens during cadmium electroplating may be as high as that introduced during severe cathodic charging and that sometimes more hydrogen is introduced during pickling or cathodic cleaning prior to electroplating than is introduced during the actual plating process.

Cadmium plating is widely used by the aircraft industry to provide galvanic protection against corrosion to steel. However, as a result of failures attributed to hydrogen-stress cracking and the possibility that additional failures might occur in ultrahigh-strength steel components, the Air Force, a few years ago, prohibited the use of cadmium electroplating of certain steels having strengths greater than 220,000 psi. Thus, it was necessary for manufacturers to resort to other methods of providing corrosion protection that were inferior to cadmium electroplating. As a result, many studies of electroplating processes in general and of cadmium electroplating processes in particular have been conducted to determine if one or more processes could be used safely for electroplating ultrahigh-strength steels.

Several approaches have been tried in an attempt to develop nonembrittling plating procedures. Some of these are:

- (1) Deposition of thin, porous plates at high current density. The porous plates would facilitate the subsequent removal of hydrogen by baking.
- (2) Plating from organic baths to prevent hydrogen deposition.
- (3) Plating from 100 percent cathodically efficient electrolytes to prevent hydrogen codeposition.
- (4) Suppression of hydrogen formation in aqueous electrolytes by bath additions.
- (5) Multiple-step plating with baking treatments between the steps to remove hydrogen.
- (6) Vacuum-evaporated coatings.

All these approaches have certain drawbacks which, depending on the process, include incomplete embrittlement relief, poor plate quality, excessive cost, and strict process-control requirements which make commercial setups very difficult.

Before discussing some of the investigations, several of the important factors affecting hydrogen deposition on and entry into steel from electroplating baths will be briefly discussed.

As an unavoidable electrode reaction occurring simultaneously with electrodeposition of the metallic coating from aqueous solutions, hydrogen ions are formed at the cathode. The product of a second reaction or of a series of reactions is atomic hydrogen which can either enter the metal in the atomic form or recombine and evolve as molecular hydrogen. Atomic hydrogen deposited on and subsequently absorbed into high-strength-steel parts may reduce ductility or increase susceptibility to hydrogen-stress cracking under conditions of sustained tensile loading.

The most common method for estimating the hydrogen input to a workpiece during electrolysis consists of determining the efficiency of the plating bath. By comparing the weight of metal actually deposited with that predicted from the plating current and time by Faraday's law, a measure of the efficiency of the plating bath being monitored is obtained. Efficiencies of 99.8 percent have been reported. If it is assumed that the remaining 0.2 percent of the plating current deposits hydrogen instead of metal, the amount of hydrogen deposited at a plating current density of 50 amperes per square foot is approximately 6×10^{17} hydrogen atoms per square foot per second. This method of estimating hydrogen entry is relatively inaccurate, and other drawbacks have been pointed out by McGraw, et al⁽⁴⁰⁾, as a result of their study of hydrogen entry into metals during chemical and electrochemical processing.

Although the efficiency of a plating bath determines the amount of hydrogen available for absorption by the metal, the amount of hydrogen actually absorbed by the metal is more important. The absorption of hydrogen from electroplating baths is controlled by factors other than bath efficiency, the most important being the amount of hydrogen absorbed on the metal surface. It has been shown that the cyanide ion (CN^-) is strongly chemisorbed during cathodic polarization of the steel surface, and it effectively retards the recombination rate of simultaneously adsorbed hydrogen atoms.⁽⁴¹⁾ The chemisorption increases rapidly with polarization time, and this results in a rise in the hydrogen coverage and creation of a steep hydrogen concentration at the steel surface. Other bath contaminants such as arsenic, phosphorus, and sulfur can also act as embrittlement promoters, or accelerators. Also, hydrogen coverage of the cathode surface in acidic solutions appreciably exceeds that in alkaline solutions.

The electrodeposited metal plate also influences the hydrogen entry rate and permeation rate, and also the resulting embrittlement. If the electrodeposited metal has a lower permeability than the basis metal, it would be expected that during a rather short initial period of electrodeposition, resulting in an extremely thin plated layer, the rate of hydrogen permeation would be primarily determined by the permeability of the iron itself. However, throughout a second phase of electrodeposition, the permeation would be controlled predominantly by variables such as hydrogen coverage and the permeability and barrier effectiveness of the electrodeposited coating.⁽⁴¹⁾ Work by Johnson, Schneider and Troiano⁽⁴²⁾ showed that the ductility of nonbaked cadmium-plated steel specimens was independent of plate thickness, which indicated that hydrogen enters the steel only during the first few minutes of plating and cannot enter after

a critical thickness of cadmium has been deposited. They suggested that with more than the critical amount of cadmium the plate acts as a barrier to hydrogen entry and also to outgassing during subsequent baking. Devanathan⁽⁴¹⁾ showed that the amount of hydrogen permeating thin Armco iron membranes during cadmium electroplating from a cyanide bath increased rapidly in the first few minutes of plating and then decreased gradually until the permeation rate became insignificant. The permeation during electrodeposition from an amino butyrate bath was considerably lower. This behavior was attributed to the higher recombination rate of hydrogen atoms as well as the barrier effect of the cadmium. The low permeation during plating from the fluoroborate bath was attributed to the low steady-state hydrogen coverage and the barrier action of the electrodeposit.

From the results of various experimental programs that will be discussed in the following paragraphs, it appears that the porosity of the electrodeposit also influences hydrogen embrittlement. Porous plates allow the hydrogen to be more easily removed from the base material during postplating aging or baking treatments.

Cotton⁽⁴³⁾ studied the hydrogen embrittlement of five aircraft-quality steels plated in three cyanide cadmium baths (a standard bath and two high-efficiency baths), three electroless nickel baths (one alkaline and two acid types), and a single hard-chromium bath of traditional composition. The five steels were AMS 6427 (AISI 4330), AMS 6407, AMS 6418, AISI 4340, and 4340-1.5Si heat treated to strength levels in the range of 220,000 to 300,000 psi depending on the nature of the steel. The compositions were as follows:

Chemical Composition of Steels					
Constituent	AMS 6427 Steel	AMS 6407 Steel	AMS 6418 Steel	AISI 4340 Steel	4340-1.5Si Steel
Carbon	0.30	0.28	0.28	0.42	0.38
Manganese	0.88	0.74	1.28	0.78	0.46
Silicon	0.30	0.62	1.40	0.21	1.64
Nickel	1.80	2.08	1.75	2.05	2.05
Chromium	0.86	1.15	--	0.85	0.98
Molybdenum	0.45	0.44	0.38	0.29	0.36
Phosphorus	0.014	0.017	0.024	0.026	0.010
Sulfur	0.014	0.013	0.010	0.011	0.017
Vanadium	0.08	--	--	--	0.06
Aluminum	--	--	--	--	0.095

Static loading tests were used, and the criterion for nonembrittlement was the ability of specimens given the same treatment to withstand a load of 75 percent of the notched ultimate tensile strength for 150 hours without failure. After being plated, all of the specimens were baked at 375 or 550 F for various periods, ranging from 3 to 23 hours.

Cotton found that all the materials were susceptible to delayed brittle failure after cadmium plating from the various baths. The use of brighteners in the cadmium baths increased hydrogen embrittlement, presumably by decreasing the porosity of the deposits so that hydrogen could not be removed effectively during the baking operation. The observed decrease in embrittlement resulting from the use of high-efficiency baths at high current density was thought to be due in part to the decreased plating time and in part to the increased plate porosity which could be expected at rapid plating rates. Cotton listed the steels in order of increasing resistance to hydrogen embrittlement

caused by cadmium plating as follows (strength level in parentheses): AISI 4340 (260-280 ksi), AMS 6427 (AISI 4330)(220-240 ksi), 4340-1.5Si (270-300 ksi), AMS 6407 (220-240 ksi), AMS 6418 (220-240 ksi). At these high strength levels, there was no consistent relationship between susceptibility to damage and strength level. These results showed that factors other than strength level and ductility of the steel are also important in determining the susceptibility of a steel to hydrogen damage. The silicon-modified 4340 steel (1.5% Si) was more resistant to hydrogen-stress cracking than was the standard AISI 4340 steel, even though the strength level of the former was slightly higher. Of particular significance is the finding that the 4340-1.5Si steel at the 270 to 300-ksi strength level was more resistant to hydrogen-stress cracking than was the AMS 6427 (4330) steel at the 220 to 240-ksi strength level. For the three steels with 0.28 to 0.30 percent carbon used at the 220 to 240-ksi strength level, the high-silicon AMS 6418 steel (Hy-Tuf; 1.40% Si) was more resistant than were the steels of lower silicon content. Thus, it appears that silicon imparts a certain measure of resistance to hydrogen-stress cracking. In the review of the DMIC publications, it was shown that silicon additions reduce the diffusivity of hydrogen in α -iron.

Cotton's data for specimens plated with chromium or electroless nickel cannot be compared directly with those samples plated with cadmium because of differences in baking temperature. Hard-chromium plating of AMS 6427 (AISI 4330) steel (220 to 240-ksi strength range) and AISI 4340 (260 to 280-ksi strength range) resulted in the steels being susceptible to hydrogen-stress cracking. The minimum stress for failure in the test used was dependent upon the baking time. After a 23-hour bake at 375 F, hydrogen-stress cracking occurred only at stresses in excess of 90 percent of the notched tensile strength. Hard-chromium plating of 4340-1.5Si steel (270 to 300-ksi strength level) which had received a 3-hour postplate bake at 550 F resulted in delayed failure only when sharp-notched specimens ($K_t = 5.7$ instead of 3.2) were used and only for stress levels somewhat higher than 90 percent of the notched tensile strength.

Electroless nickel plating of AISI 4340 steel (260 to 280-ksi strength level) from an aqueous bath resulted in delayed failure under static-loading conditions only at applied stresses in excess of 90 percent of the notched tensile strength of the unplated specimens. Even though this is a nonelectrolytic process, gas evolution accompanies the replacement reaction in which the more active iron replaces nickel in the solution. The lower critical stress for failure for acid electroless nickel appeared to be about 90 percent of the notched tensile strength for parts baked 23 hours at 375 F. Electroless nickel plating of 4340-1.5Si steel (270 to 300-ksi strength level) which had received a 3-hour postplate bake at 550 F resulted in hydrogen-stress cracking only when sharp-notched specimens ($K_t = 5.7$ instead of 3.2) were used and only at stresses somewhat above 90 percent of the notched tensile strength.

Geyer, Lawless, and Cohen⁽⁴⁴⁾ studied various cadmium-plating systems to determine if one or more could be safely used for electroplating ultrahigh-strength steel. They used sustained-load tests employing notched specimens of AISI 4340 steel heat treated to the 290,000-psi tensile-strength level (notched tensile strength 435,000 psi). The criterion for acceptance of a plating system was that 4 of 4 specimens withstand an applied stress of 300,000 psi for the duration of the test. All plated specimens were baked at 375 F, generally for 23 hours, prior to testing.

The plating baths were conventional cyanide, high-efficiency cyanide, sulfamate, and fluoborate. The conventional cyanide bath, with and without brightness, and the fluoborate bath with various additions to change the porosity of the deposit produced

embrittlement using the criteria that if one specimen failed at a load of 300,000 psi the entire group was to be considered as having failed. The high-efficiency cadmium cyanide plating bath without a brightener produced no detrimental hydrogen embrittlement in specimens that were baked for 23 hours at 375 F after plating. However, when a brightener, which actually increased the cathode efficiency, was added to improve the coating appearance, a plated specimen failed after 33 hours when loaded at 300,000 psi. It appeared that the significant differences in the two deposits with respect to hydrogen embrittlement were the structure of the cadmium electrodeposits. The more porous, granular structure allowed more hydrogen to be driven out during the post-plating baking treatment.

When the sulfamate bath (cathode current efficiency of approximately 100 percent) was used, a crystalline electrodeposit was obtained and none of the specimens failed. However, addition of an agent to produce a ductile, white, fine-grained deposit caused all the specimens to be embrittled. Again, the only difference was in the structure of the electrodeposit.

As a result of their studies, these investigators proposed that the residual hydrogen embrittlement as a result of electroplating is a composite effect depending on both the cathode current efficiency and the physical structure of the cadmium electrodeposit.

To determine the barrier effect of vacuum-deposited cadmium, Geyer, et al,⁽⁴⁴⁾ electroplated a vacuum-metallized specimen with cadmium from a fluoborate bath that contained peptone. The specimen was not baked after plating and it failed upon loading at 300,000 psi. Therefore, the vacuum-deposited cadmium did not prove to be a barrier to hydrogen penetration during subsequent cadmium electrodeposition.

These investigators also evaluated an SAE H-11 (5Cr-Mo-V) steel heat treated to 280,000-psi ultimate tensile strength. The fluoborate, high-efficiency cadmium, and conventional cadmium electroplating processes did not cause detrimental hydrogen embrittlement of the H-11 steel. This behavior was ascribed to reduced susceptibility to hydrogen embrittlement of the H-11 steel. As was discussed in the review of the DMIC publications, chromium reduces the diffusivity and permeation of hydrogen in body-centered cubic iron alloys.

A cooperative testing program was conducted by Aerospace Research and Testing Committee Project 6-61⁽⁴⁵⁾ to compare the hydrogen-embrittlement characteristics of several plating systems that were reported to be nonembrittling. With these plating systems, the investigators attempted to reduce hydrogen entry and/or to promote subsequent removal of hydrogen from plated steel in the following ways:

- (1) Porous deposits and subsequent baking to remove and/or redistribute the hydrogen absorbed.
- (2) High-efficiency (low-hydrogen-producing) bath with subsequent baking.
- (3) Suppression of hydrogen formation by additives.
- (4) Organic baths with no hydrogen formation.
- (5) Organic brush-plating baths.

These plating systems were evaluated by sustained-load tests employing notched tensile specimens (0.003-inch notch root radius) and Douglas ring specimens made of AISI 4340 steel (280,000-psi tensile strength).

The results of the tests employing the Douglas ring specimens were inconclusive, as these specimens were not sufficiently sensitive to detect embrittlement except in the cases of severe embrittlement. The results of the tests employing the notched tensile specimens were as follows (the lower critical stress for failure is shown in parentheses):

- (1) Triethanolamine (260,000 psi) and Boeing BAC 5718 (270,000 psi). Very little embrittlement shown. Lower critical stress approximately 10,000 psi below upper critical stress. The triethanolamine system employs no baking treatment. The Boeing BAC 5718 process employs a 23-hour bake at 375 F.
- (2) Lockheed Type II Class C (245,000 psi) and Douglas K.2 Cyanide (225,000 psi). Only slightly more embrittlement shown than the processes listed under (1). The Lockheed process employs an 8-hour bake at 375 F, while the Douglas process is followed by a 23-hour bake at 395 F. Although the Dalic brush plating appeared to be in this class, there were not sufficient data to prove this.
- (3) Cleveland Pneumatic Tool, CPT 8206 (215,000 psi). This process is followed by a 23-hour bake at 380 F - 400 F.
- (4) The remaining plating systems showed lower critical stresses in the range from 185,000 psi to 65,000 psi, as follows:
 - Titanium Cadmium Plating (185,000 psi)
 - Grumman Nonaqueous Plating, dimethylformamide (175,000 psi)
 - Lockheed Type II Class B (110,000 psi)
 - Douglas Fluoborate (65,000 psi)

In both the titanium-cadmium plating process and the Douglas fluoborate process, the specimens were stripped after initial plating and replated. It was not known if this process was responsible for the lower values of lower critical stress obtained from these systems; however, it was suspected that it had an influence on them.

Of the five top-rated systems, one was an organic system (triethanolamine solution). The remaining four were aqueous solutions operated at current densities from 50 to 70 amps/ft². None of these solutions contained brighteners. Of these processes, only one, the Lockheed process, employed an acid etch prior to plating. The three top-rated systems evaluated in this work had values of lower critical stress in excess of the notched tensile strength of unplated specimens. Beneficial effects of abrasive blasting used by all three processes prior to plating may be an explanation for this observed behavior.

More recent investigations of the titanium-cadmium plating process and the Grumman nonaqueous plating process have shown both processes to be nonembrittling under the testing conditions employed. Gahnberg⁽⁴⁶⁾ evaluated the titanium-cadmium (Delta) plating process using sustained-load tests of notched specimens of 4330 M steel

(220 to 240-ksi strength range) and AISI 4340 steel (260 to 280-ksi strength range). Specimens of these two materials withstood sustained load at a stress equal to 75 percent of their respective notched tensile strengths for periods up to 700 hours, without failure. Also titanium-cadmium-plated panels withstood more than 2,600 hours of intermittent salt-spray exposure without any trace of corrosion products.

The titanium-cadmium plating solution, developed by the Japanese, is similar to that of a conventional cadmium-plating bath, except that metallic titanium is held in suspension in the plating system. There are two basic principles involved in the titanium-cadmium plating process. First, since titanium has a higher affinity for hydrogen than does steel, most of the hydrogen evolved at the cathode during the plating process is absorbed by the titanium in the form of a stable titanium hydride. Second, the "as-deposited" plate contains between 0.15 and 0.5 percent titanium. This titanium acts as a hydrogen scavenger during the postplate baking cycle to absorb any hydrogen that entered the steel during the plating process. Gahnberg pointed out that this plating system is being used in some service applications; a commercial jet airliner is now operating with landing gear and many heavy structural components which have been plated with the titanium-cadmium (Delta) process.

Micillo⁽⁴⁷⁾ presented the results of an evaluation of the Grumman nonaqueous, dimethylformamide/cadmium iodide plating process. The advantage of the DMF process is that it avoids codeposition of hydrogen at the cathode. This is done by using mechanical cleaning procedures and by using organic solvents instead of conventional aqueous solutions which carry ionizable hydrogen. The results of sustained-load testing of notched AISI 4340 bars (280,000-psi strength level) cadmium plated with the DMF process showed no failures in 18 specimens loaded to 75 percent of the notched tensile strength of unplated material and no failures in 5 specimens loaded to 90 percent of the notched tensile strength. None of these specimens were baked after plating. For comparison, two specimens plated from a conventional cyanide bath failed at stresses of 75 percent of the notched tensile strength after 13 hours, even though they had been baked for 23 hours at 375 F after plating. The adhesion and corrosion protection obtained with cadmium deposited from the DMF bath compared favorably with deposits obtained from the aqueous cyanide plating bath.

Micillo⁽⁴⁸⁾ tested C-ring specimens of AISI 4340 steel and AMS 6427 (AISI 4330) steel (220-ksi and 215-ksi yield strengths, respectively) that were plated with a 0.0001-inch layer of cadmium, baked 1 hour at 375 F, and then plated to a thickness of 0.0005 inch of cadmium. Prior to testing, the specimens were baked 23 hours at 375 F. All the specimens survived 646 hours at stresses equal to 90 percent of their yield strengths.

Beck and Jankowsky⁽⁴⁹⁾ investigated the effectiveness of Watts-type bright nickel and pyrophosphate copper (both electroplated coatings) as undercoats in minimizing the embrittlement induced by overplating with cyanide cadmium and conventional chromium electroplates. Both undercoats resulted in some decrease in the susceptibility to delayed failure under sustained load when the undercoats were thick enough. Since other work purportedly had shown that neither hydrogen atoms nor protons diffuse through thin nickel layers,* Beck and Jankowsky concluded that the effect of nickel and other metallic undercoats is the result of their action as diffusion barriers, and the barrier

*However, as is discussed in the review of the DMIC reports, other investigators have shown that nickel is an endothermic occluder of hydrogen, and the solubility of hydrogen in nickel is reported to be several times greater than that in iron for the same temperature and pressure.

effectiveness apparently is related to the thickness of the undercoat. They suggested that deficiencies in the effectiveness of the barrier coating, as revealed by the sensitive delayed-failure test, are the result of plating imperfections.

Forney and Katlin⁽⁵⁰⁾ evaluated hydrogen embrittlement of SAE 4140 and SAE 4340 steels at the 270,000, 230,000, and 180,000-psi strength levels and AISI Type H-11 steel at the 270,000-psi strength level from cadmium cyanide, cadmium fluoborate, chromium, Watts nickel, and acid and Alaline electroless nickel plating baths. Their results from sustained-load tests using notched specimens (0.003-inch notch root radius) showed that hydrogen-stress cracking occurred for specimens above the 230,000-psi strength level when plated in the fluoborate cadmium bath and above the 180,000-psi strength level when the cyanide-cadmium bath was used. Embrittlement of SAE 4140 and 4340 steels occurred above the 230,000-psi strength level when they were chromium plated. The minimum stress for failure for SAE 4140 steel (270,000-psi strength level) without any relief treatment was approximately 85,000 psi for cadmium deposited from the cyanide bath and approximately 15,000 psi for electro-deposited chromium. The use of a thin hydrogen-free barrier plate of cadmium or nickel to inhibit the diffusion of hydrogen from subsequent overplating operations did not prevent embrittlement. The H-11 steel was plated with a thin layer of nickel and then cadmium plated to a final thickness of 0.0005 inch. The samples showed no evidence of embrittlement after baking for 30 minutes at 600 F. With this baking treatment, the cadmium and nickel fused to form a protective alloy coating.

In another study of the embrittling effects of cyanide cadmium plating on Type H-11 steel, Jankowsky⁽⁵¹⁾ found that the loss in tensile strength and loss in ability to carry a sustained load increased as the tensile strength of the material increased, just as other investigators have found for other alloy steels. Notched tensile specimens tempered at 1125 F (200,000-psi ultimate tensile strength) showed no loss in tensile strength but a 14.5 percent loss in their ability to carry a sustained load. Specimens tempered at 1075 F (240,000-psi ultimate tensile strength) showed a 15.2 percent loss in tensile strength and a 21.6 percent loss in ability to carry a sustained load. None of the specimens were baked prior to testing.

Beck and Jankowsky⁽⁵²⁾ attempted to solve the hydrogen-embrittlement problem by trying to find a high-strength steel with greatly reduced susceptibility to embrittlement. They found that both the notch sensitivity and composition of the steel (particularly chromium content) have a marked influence on susceptibility to hydrogen embrittlement. Increasing the chromium content up to 8 percent progressively reduced hydrogen embrittlement (see Figure 25). Beyond 8 percent, the beneficial effect of chromium in reducing susceptibility to hydrogen-stress cracking appeared to be offset by a marked decrease in notch strength/ultimate tensile strength ratio. Vacuum melting also appeared to be beneficial. Sustained-load tests employing notched tensile specimens which had been bright-cadmium plated were used in this evaluation. The steels evaluated were air- and vacuum-melted AISI 4340, air- and vacuum-melted H-11, ausformed H-11, ausformed AISI 4140, X-8 (an experimental 8 percent chromium steel) and X-10 (an experimental 10 percent chromium steel). Figures 26 and 27 summarize the results of this investigation. Note the excellent behavior of the X-8 steel, an experimental 8 percent chromium alloy. Also, vacuum melting lowered the susceptibility to delayed failure caused by electroplating for both steels so treated (AISI 4340 and H-11 steels).

Because chromium plating was limited to steels heat treated to tensile strengths below 200,000 psi since problems of embrittlement were encountered at higher

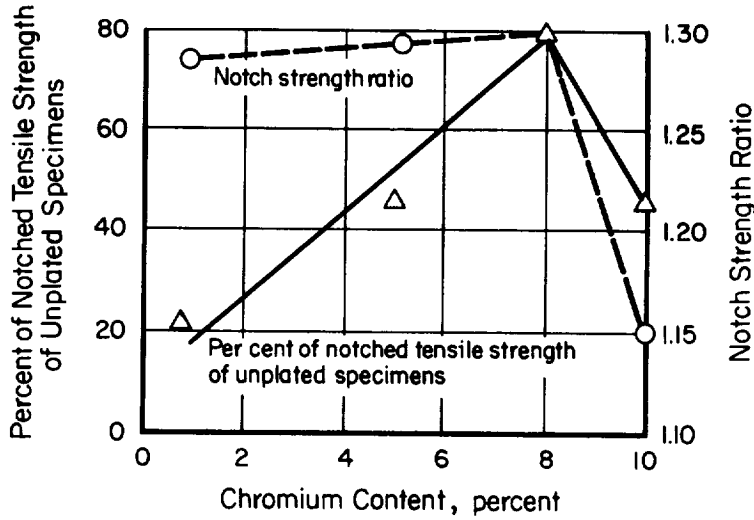


FIGURE 25. INFLUENCE OF CHROMIUM CONTENT ON THE NOTCH STRENGTH RATIO AND LOWER CRITICAL STRESS (EXPRESSED AS PERCENT OF NOTCHED TENSILE STRENGTH OF UNPLATED SPECIMENS)⁽⁵²⁾

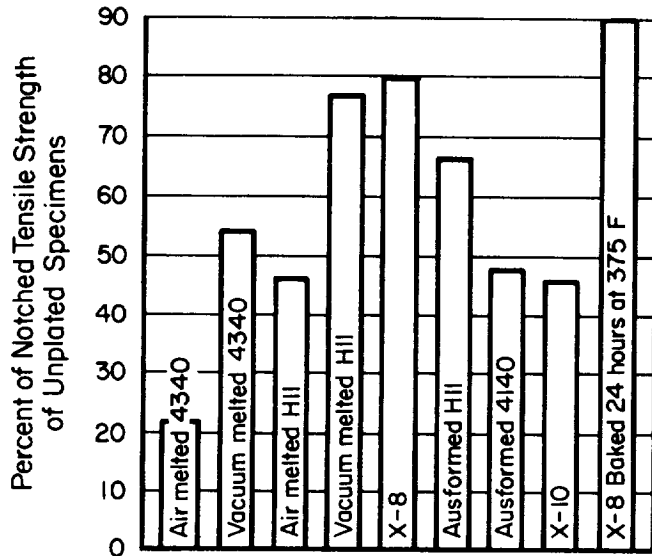


FIGURE 26. VALUES OF LOWER CRITICAL STRESS (500 HR) OF STEEL SPECIMENS CADMIUM PLATED IN A CYANIDE BATH⁽⁵²⁾

The values are presented as percent of notched tensile strength of unplated specimens. Vacuum melting has lowered the susceptibility to embrittlement caused by electroplating. Note the excellent behavior of X-8 steel, an experimental 8 percent chromium alloy.

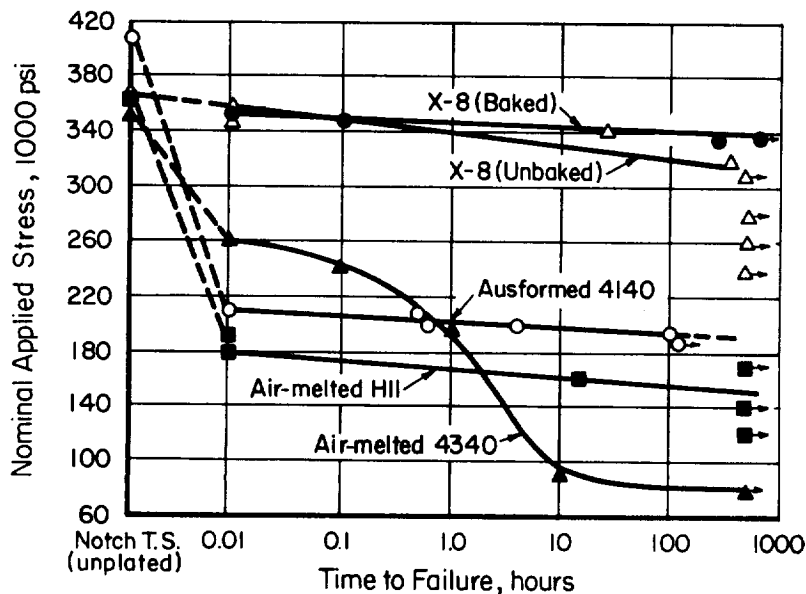


FIGURE 27. NOTCHED TENSILE STRENGTHS OF UNPLATED STEELS AND FAILURE TIMES OF THEIR CADMIUM-PLATED COUNTERPARTS TESTED UNDER SUSTAINED LOADS⁽⁵²⁾

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strengths, Krieg⁽⁵³⁾ investigated the effects of a hard, high-chromium-alloy electroplating process on AISI 4340 steel heat treated to the 220,000 to 240,000-psi strength range. Notched tensile specimens were plated by three different vendors. The plated specimens from each vendor were divided into two groups; one group was tested in sustained load in the as-received condition, while the other group was given an embrittlement-relieving treatment at 375 F for 24 hours before testing. None of the specimens which were tested under sustained loads in the as-received condition withstood the stress for more than 5 hours when loaded to 75 percent of the notched tensile strength of unplated specimens. All of the specimens which were given the embrittlement-relieving baking treatment before the test withstood 100 hours at stresses of 75 percent and 90 percent of the notched tensile strength. On the basis of the test results, the application of hard, high-chromium-alloy plate to AISI 4340 steel heat treated to the 220,000 to 240,000-psi strength range resulted in serious embrittlement of the steel. However, a subsequent 24-hour baking treatment at 375 F was sufficient to relieve the embrittlement under the test conditions used.

More recently the 18Ni maraging steels have been evaluated for susceptibility to hydrogen embrittlement resulting from cadmium, chromium, and nickel plating. Trobocco⁽⁵⁴⁾ found that the notched tensile strength of 250-grade and 300-grade maraging steel was reduced slightly as a result of cadmium (cyanide bath) plating. However none of the plated specimens failed when statically loaded at stresses up to 90 percent of the notched tensile strength for times up to 500 hours.

DiBari⁽⁵⁵⁾ studied the susceptibility of 18Ni maraging steel (250-grade) to hydrogen embrittlement caused by nickel, nickel-chromium, and cadmium plating. Nickel and cadmium plating appeared to have little or no effect on the notch-tensile-strength values. Four nickel-plated specimens sustained stresses of 90 and 92 percent of the notch tensile strength without failure. The duration of the tests varied from 166 hours to 362 hours. However, heavy chromium plating over the nickel (0.5 mil of nickel + 1.0 mil of chromium) caused the specimen to break on loading at 81 percent of the notch tensile strength. Nickel/chromium plated specimens baked at 450 F for 24 hours before testing withstood loads of 90 percent of the notch tensile strength for more than 150 hours without failing.

DiBari also studied the effect of processing variables on the gas content of maraging steels using panels plated with 2.0 mils of nickel and 4.0 mils of chromium. The results of gas analyses at various stages during processing indicated that pretreatment up to and including the acid nickel chloride strike increased the hydrogen content by about 1.0 ppm. Subsequent nickel plating gave a further increase, but it was less than 1.0 ppm. The hydrogen content increased by about 20 ppm when the specimens were plated with chromium. A large increase in oxygen content also was observed.

The 18Ni maraging steels are not immune to hydrogen embrittlement, as was shown by the nickel/chromium-plated steel. However the 18Ni maraging steel appears to be considerably less susceptible to hydrogen embrittlement than is SAE 4340 steel under plating conditions which introduce small amounts of hydrogen. Since the maraging steels are not immune to embrittlement by hydrogen, baking after plating appears to be essential to guard against accidental embrittlement.

Summarizing the results of the numerous investigations of the hydrogen embrittlement induced by various plating processes into a few general conclusions is very difficult because of the many variables involved.

Conventional plating processes have been shown to cause hydrogen-stress cracking of many high-strength steels. At the higher strength levels (above about 180,000-psi tensile strength) susceptibility to hydrogen-stress cracking has persisted even after long postplating baking treatments. The data indicate that steels with tensile strengths below about 180,000 psi can be electroplated in conventional baths without danger of hydrogen-stress cracking, provided that they are given a suitable relief treatment after plating.

Some investigators have reported that some plating processes are nonembrittling. Among these so-called nonembrittling processes are the cadmium triethanolamine process, the cadmium dimethylformamide process, and the titanium-cadmium (Delta) process. However, until the basic mechanism of hydrogen embrittlement of steels is completely understood and quantitative data with respect to hydrogen in steel become available, it is meaningless to merely state that a process is embrittling or nonembrittling. Variables which also must be considered are the composition of the steel used to evaluate the process, the strength level of the steel, the stress level used to determine the degree of embrittlement, the test method, and the ability of the coating to allow embrittlement relief. If these variables are fixed, then it could be stated that a process is embrittling or nonembrittling, but only for the fixed conditions.

In addition to considering the plating process itself, the entire processing history of the material used to evaluate the process must be considered. Sufficient hydrogen may be picked up during heat treating, pickling, or cathodic cleaning prior to electroplating to render the material susceptible to hydrogen-stress cracking regardless of the embrittling characteristics of the plating process. Therefore, all these preplating treatments must be evaluated and their ability to induce embrittlement recognized. Those processes which introduce hydrogen should be eliminated or placed under strict control to eliminate hydrogen pickup.

Hydrogen Embrittlement of Nickel-Base Alloys

Because many alloy systems had been investigated and hydrogen embrittlement had been found only in body-centered cubic transition metals, a number of investigators inferred that no face-centered cubic metal can be embrittled by hydrogen. However, Eisenkolb and Ehrlich⁽⁵⁶⁾ discovered that nickel could become embrittled by hydrogen. Later, Blanchard and Troiano⁽⁵⁷⁾ verified the embrittlement of nickel and also found that certain nickel-base, nickel-iron alloys were embrittled by hydrogen. The purpose of their study was to determine whether the embrittlement of nickel was of the same nature as that of steel and to determine the effect of alloying on the magnitude of the embrittlement in nickel. The materials studied were as follows:

Material	Composition, percent		
	Ni	Cr	Fe
"A" Nickel	99.4	--	0.15
72Ni-28Fe	72.7	--	27.2
51Ni-49Fe	51	--	49
Nilvar	36	--	64
Nichrome I	60	16	24
Nichrome V	80	20	--
25-20 stainless	19.7	24.9	52.8

Both thermal and cathodic charging were used to introduce hydrogen into the alloys. Thermal charging was used for the 25-20 stainless steel in which the diffusion rate of hydrogen is low at room temperature; the other alloys were cathodically charged. The investigators found that the nickel and some of the nickel-base alloys were embrittled by hydrogen when cathodically charged for several hours at a high current density. This embrittlement was indicated by a loss of ductility in the tensile test. None of the materials failed by hydrogen-stress cracking. Studies of the strain-rate dependence, the temperature dependence of the embrittlement, and the recovery of ductility upon aging showed that this embrittlement was of the same type as that of ferritic and martensitic steels. The observed embrittlement was a maximum for pure nickel and nil for the 51Ni-49Fe alloy, Nilvar, and 25-20 stainless steel.

In another study, Schaller and Troiano⁽⁵⁸⁾ found that cathodic charging of nickel and nickel-base alloys resulted in the formation of a second face-centered cubic phase, termed beta. The formation of this phase led to a decrease in the driving force for diffusion and caused a high surface concentration of hydrogen. This surface layer was embrittled and exhibited the inverse strain-rate behavior and the temperature behavior associated with hydrogen embrittlement. At low strain rates and intermediate temperatures, cracks formed in the surface layer and resulted in a loss of ductility. The behavior closely paralleled that found in other studies of brittle skins, except for the temperature and strain-rate effects.

The beta phase played a role through its influence on hydrogen distribution, and there is some evidence that it may be a sufficient condition for embrittlement in these alloys. Specimens tested under sustained load did not fail. This apparent absence of delayed failure was attributed to insufficiently deep penetration of hydrogen, that is, the beta phase constituted only a thin, surface layer.

More recent studies by Troiano and associates^(59,60) have shown that hydrogen can produce delayed brittle failure in a face-centered cubic nickel alloy. The material studied in these investigations was a high-strength alloy with a nominal composition of 66 nickel-30 copper-3 aluminum, commercially designated as K-monel. The alloy was heat treated to an ultimate tensile strength of 185,000 psi. The specimens were charged cathodically in a 4 percent sulfuric acid solution poisoned with sodium arsenite which was used at a current density of 1.0 amp/in.². The electrolyte was maintained at 176 F, and the charging time was 96 hours. After cathodic charging, the majority of the samples were baked 4 minutes at 910 F in air and then were water quenched. Some of the specimens used in the delayed-failure study and in tensile testing were plated with cadmium in a sodium cyanide-cadmium oxide bath after baking.

The sustained load tests were conducted in the temperature range of 350 to 500 F where the diffusivity of hydrogen in the face-centered cubic lattice is approximately the same as it is in body-centered cubic iron at room temperature. Delayed failure in the hydrogenated-and-baked alloy was observed at 350, 400, and 500 F over a relatively wide range of applied stress, 160,000 to 225,000 psi. Failure did not occur in hydrogen-free specimens under load for several hundred hours more than the hydrogenated specimens. In this instance, hydrogen-free refers to both the uncharged material and hydrogenated material which was subsequently baked at 212 F to remove hydrogen. The absence of delayed failure coincident with hydrogen removal indicates that the hydrogen-embrittlement phenomenon is completely reversible up to the point where permanent damage occurs.

The delayed-failure curves observed for the hydrogenated 66Ni-30Cu-3Al alloy have the same general features which characterize delayed brittle failure in high-strength steel: an upper critical stress which decreases with increasing temperature, a range of time-dependent failure where the failure time increases with decreasing temperature, and a lower critical stress which decreases with increasing temperature.

The results of these investigations show that nickel and nickel-base alloys are susceptible to hydrogen embrittlement as indicated by a loss in tensile ductility and, also, under the proper laboratory conditions they are susceptible to hydrogen-stress cracking. However, no data were found to indicate that hydrogen embrittlement of nickel-base alloys will result from normal processing operations.

The Effect of Hydrogen on Titanium and Titanium Alloys

The effects of hydrogen on titanium and titanium alloys have been reviewed in detail in TML Report 100.⁽⁶¹⁾ In the present report, some of the more important factors will be discussed briefly, and more recent information will be reviewed.

The factors of greatest significance in determining the behavior of hydrogen in titanium and titanium alloys are the temperature dependence of hydrogen solubility in alpha and beta titanium, hydrogen partial pressure, and alloy composition. These factors control absorption, embrittlement, degassing, and many other phenomena observed in hydrogen-containing titanium alloys.

At elevated temperatures, hydrogen is considerably more soluble in beta than in alpha titanium. The relative solubilities in the vicinity of room temperature have not been determined exactly; however, it has been estimated that the hydrogen solubility decreases quite rapidly in beta as well as alpha titanium as room temperature is approached, such that at room temperature very little hydrogen is soluble in either phase, resulting in the precipitation of hydrides.

Certain beta-stabilizing elements, notably molybdenum, apparently tend to increase the solubility of hydrogen in beta titanium at room temperature. Small amounts of molybdenum-containing beta phase in predominantly alpha alloys raise the tolerance for hydrogen by about 100 ppm, as determined by impact tests.⁽⁶²⁾ The results of stress-rupture tests show that molybdenum also increases the tolerance for hydrogen in alpha-beta alloys.⁽⁶³⁾ Other beta-stabilizing elements, including iron, manganese, vanadium, chromium, and columbium, apparently result in a beta phase with lower solubility for hydrogen, as determined for alloys that are predominately alpha phase.⁽⁶⁴⁾ However, in alpha-beta alloys, columbium and chromium appear to increase the solubility of hydrogen in the beta phase.⁽⁶³⁾ Aluminum has been shown to increase considerably the solubility of hydrogen in alpha titanium at room temperature.⁽⁶⁵⁾ Aluminum may be effective, at least in part, because of its ability to retard precipitation of hydride on cooling. The higher solubility of hydrogen in aluminum-containing alpha titanium is apparent also in alpha-beta alloys in which the presence of aluminum reduces the tendency toward low-strain-rate embrittlement.⁽⁶³⁾

The effects of minor amounts of impurities on the titanium-hydrogen equilibrium system have been investigated in alloys prepared from sponge titanium. At high temperatures, the solubility of hydrogen in alpha titanium is reduced by interstitial

impurities; however, this effect is much less at room temperature. (65) The solubility of hydrogen in beta titanium appears to be strongly dependent on purity; here, again, impurities reduce hydrogen solubility significantly. (63)

In addition to modifying the solubility relationships, alloying titanium also changes the mode of hydride precipitation. In unalloyed titanium, the hydride assumes a random distribution throughout the alloy and the form is strongly dependent on the cooling rate. In alpha alloys containing 5 percent or more aluminum, the hydride precipitates predominantly at the grain boundaries. (66) In alpha-beta alloys, titanium hydride forms predominantly along the alpha-beta interfaces. It has been hypothesized that hydride cannot nucleate within beta titanium and that a nucleation site such as an alpha-beta interface is required. For example, in a Ti-20Mo beta alloy, 4200 ppm hydrogen was required to cause complete embrittlement, and no hydride was found in that material.

Diffusion of Hydrogen in Titanium

Hydrogen is dissolved interstitially in titanium, and it diffuses quite rapidly through the metal at elevated temperatures. The diffusion coefficient (D) for high-purity alpha titanium was found to vary from 0.6×10^{-5} cm²/sec to 6.4×10^{-5} cm²/sec in the temperature range 930 F to 1510 F. (67) The diffusion rate of hydrogen in beta titanium is higher than that in alpha titanium. The diffusion coefficient in beta is reported to vary between 0.5×10^{-4} cm²/sec at 1200 F and 1.4×10^{-4} cm²/sec at 1830 F. (67) The calculated values for D_0 and the activation energy (E) for beta titanium were 1.95×10^{-3} cm²/sec and 6640 cal/mole, respectively. For comparison, the calculated value of D at 1290 F for alpha titanium was 6.24×10^{-5} cm²/sec.

Measurements made during degassing studies can be used to approximate diffusion coefficients since, in the absence of surface effects, the degassing coefficient is reported to be equal to the diffusion coefficient. Measurements made on several titanium alloys showed that, although the activation energy (E) is similar to that for beta titanium, the diffusion coefficient is similar to that of alpha alloys, suggesting that alloying blocks the free movement of hydrogen through the metal. (63)

Absorption of Hydrogen by Titanium

Titanium is an exothermic occluder of hydrogen and, thus, belongs to the group of metals that has the largest capacity to absorb hydrogen and still retain metallic characteristics. The endothermic occluders of hydrogen (such as iron and nickel) take up hydrogen only in small quantities, even at elevated temperatures where the solubility of hydrogen is greatest in this class of materials. The exothermic occluders, however, absorb hydrogen in much larger quantities, forming alloys of greater complexity which exhibit unmistakable solid solutions and one or more secondary phases. These exothermic metals sometimes are called "hydride formers". The titanium-hydrogen phase diagram for 1-atmosphere hydrogen pressure is shown in Figure 28. At elevated temperatures, hydrogen solubilities up to 49 atomic percent (1.98 weight percent) may be attained without forming a hydride.

The absorption of hydrogen by titanium is controlled by two factors, adsorption of atomic or molecular hydrogen on the surface and diffusion of the adsorbed hydrogen

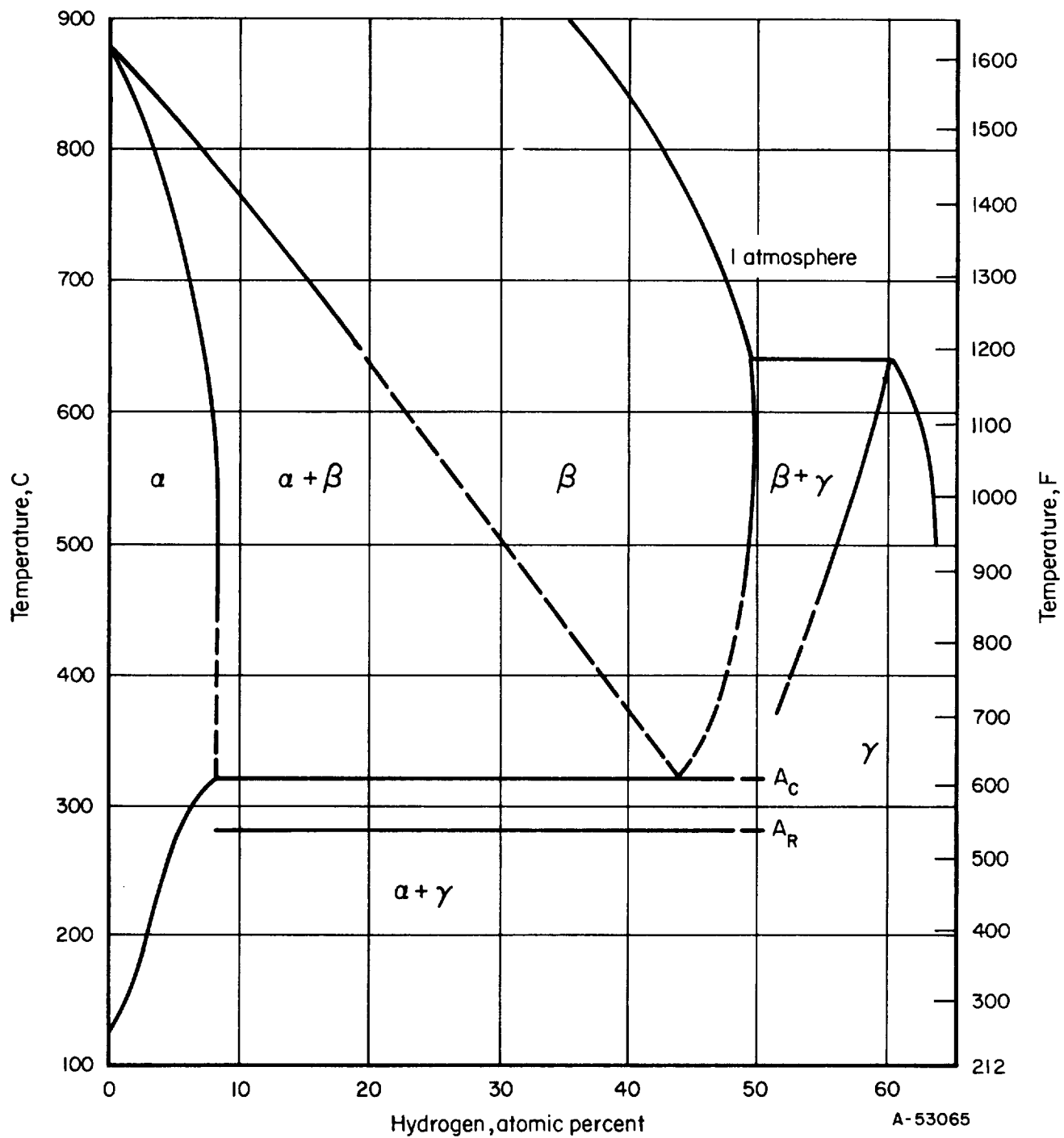


FIGURE 28. HIGH-PURITY TITANIUM-HYDROGEN EQUILIBRIUM DIAGRAM^(68,69)

into the bulk of the material. Therefore, the rate of absorption can be controlled by external (environmental) conditions, by surface properties, and by internal or bulk properties of titanium.

The most critical factor in the absorption of hydrogen by titanium is the adsorption of hydrogen on the surface. The partial pressure of hydrogen surrounding the material controls the amount of hydrogen that will enter titanium at any temperature. For example, at 1200 F, high-purity titanium should absorb no more than about 4 atomic percent hydrogen at a partial pressure of 0.001 atmosphere. The absorption of hydrogen at 535 F as a function of pressure shows a nearly linear dependence upon the square root of the hydrogen pressure, indicating that the dissociation of molecular to atomic hydrogen is occurring at the surface under these conditions.⁽⁶⁸⁾ Also, it is apparent that the rate at which hydrogen is absorbed is quite dependent on surface area, so that the amount absorbed in a given time will increase as the ratio of surface area to volume is increased.

At temperatures less than about 480 F, the absorption of hydrogen occurs very slowly at low pressures of hydrogen.⁽⁷⁰⁾ However, at 570 F, the rate of absorption is quite high. Absorption of hydrogen at room temperature at quite low pressure has been reported. The presence of an oxide film on the metal surface can considerably retard the absorption of hydrogen.

The factors within titanium that affect the diffusion rate of hydrogen also affect the absorption rate. Near room temperature, diffusion rate and solubility of hydrogen in alpha and beta are both relatively low, and the formation of hydride occurs on the metal surface. At higher temperatures, where diffusion is quite rapid and the solubility of hydrogen is greater, a visible hydride layer seldom forms and the bulk hydrogen content increases rapidly and uniformly.

Alloying generally decreases the rate of hydrogen absorption by titanium⁽⁶³⁾ and also appears to affect the minimum temperature at which hydrogen can be absorbed.⁽⁷¹⁾ Aluminum apparently retards the absorption of hydrogen quite strongly. The results of McKinsey, Stern, and Perkins⁽⁷²⁾ showed that the microstructure of titanium has a significant effect on the absorption of hydrogen. In cathodically charged specimens of predominantly alpha alloys, hydrogen absorption was limited to a thin surface layer of hydride. When a beta network was present, hydrogen penetrated much more deeply into the alloy. Acicular structures, having a more continuous beta network, showed greater absorption than equiaxed structures. Large amounts of hydrogen were absorbed in alloys containing moderate amounts of beta, with no evidence of hydride at the surface or in the alloy. One alloy (Ti-8Mn) absorbed 12,100 ppm (37 atomic percent) during cathodic charging without visible signs of hydride in the resulting structure.

Control of Hydrogen Contamination of Titanium. Because of the relative ease with which titanium absorbs hydrogen at moderate temperatures, a number of potential sources of hydrogen contamination exist. In each stage of production and fabrication, special precautions must be observed to prevent or minimize hydrogen absorption. As the technology has been advanced, most of the sources of contamination have been recognized and placed under control, so that through constant inspection and process control, severe hydrogen contamination has been virtually eliminated.

In the earlier stages of titanium production technology, the major sources of contamination were: (1) hydrogen carried into the melting furnace in the sponge and alloying additions and (2) hydrogen picked up by the massive metal during descaling and acid pickling.⁽⁷³⁾ The principal sources of hydrogen in sponge titanium are water vapor in the reaction chamber in which the sponge is produced, the hygroscopic action of small amounts of $MgCl_2$ remaining with the sponge, and acid leaching (when used).⁽⁷⁴⁾ By control of the reduction process and storage of the sponge product in a dry atmosphere, contamination of the sponge product has been appreciably reduced. Moreover, now that vacuum-melting procedures have become common, hydrogen present in sponge is removed during subsequent melting operations. Therefore, this source of hydrogen contamination has been virtually eliminated.

Because titanium is capable of absorbing hydrogen from a number of gases quite readily, considerable pickup of hydrogen during both primary and secondary fabrication might be expected, and contamination of titanium in furnace atmospheres is known to occur. Fortunately, the presence of an oxide film considerably hinders hydrogen absorption. Since an oxide film forms quite readily, trouble with hydrogen absorption is seldom encountered in neutral or oxidizing furnace atmospheres. However, in reducing atmospheres, hydrogen absorption can occur. Therefore, water vapor should be avoided in the furnace atmosphere.

Since hydrogen absorption is a surface-dependent reaction, it becomes considerably more severe as the surface-to-volume ratio increases. Thus, it becomes more important to control the furnace atmosphere as the material is reduced to thin gages. Also, it is probable, in view of previously described alloy differences, that more precautions are necessary in heating and working alpha-beta alloys than alpha alloys.

Descaling and Pickling as a Source of Hydrogen in Titanium. Perhaps the most frequent sources of hydrogen in titanium products are the descaling and pickling operations. Chemical descaling is commonly used to remove large amounts of oxide scale from titanium. One of two types of descaling processes is normally used - the oxidizing process or the reducing process.

The bath for the oxidizing process consists of about 85 percent fused sodium hydroxide and 15 percent of oxidizing agents such as sodium nitrate.⁽⁷⁵⁾ Included are such proprietary mixtures as the Virgo Salt Process and the Kolene Process. In these descaling baths, the scale is dissolved in the molten salt. Attack of the metal and hydrogen evolution are minimized, so that little difficulty with hydrogen absorption is encountered. The results of a study of hydrogen contamination in the Virgo descaling process showed no hydrogen pickup⁽⁷⁶⁾ (Table 5).

The reducing process generally employed for titanium is the Sodium Hydride Descaling Process in which 2 percent sodium hydride dissolved in molten sodium hydroxide attacks and reduces the titanium scale.⁽⁷⁵⁾ Attack of the metal continues after the scale has been removed from the metal. The large hydrogen concentration inherent in the chemical reactions in the bath leads to rapid contamination of the metal with hydrogen once the oxide scale is removed. Results of studies of hydrogen contamination occurring in the sodium hydride process are given in Table 6.⁽⁷⁶⁾ Contamination is quite severe.

Although a number of factors such as alloy composition, amount of metal removal, and surface-to-volume ratio have an effect on the pickup of hydrogen in the sodium

TABLE 5. HYDROGEN PICKUP AND METAL LOSS FOR VIRGO
DESCALING OF A-55 AND C-110M TITANIUM-
ALLOY 1/4-INCH ROD (76)

<u>Descaling Treatment</u>		Weight Loss, mg/cm ²	Hydrogen Absorption, ppm
Time, min	Temperature, F		
<u>Commercial A-55 Titanium</u> (Initial hydrogen content, 38 ppm)			
<u>Scale free</u>			
30	850	3.1	5
60	850	5.4	5
5	930	2.3	9
15	930	6.1	4
30	930	7.5	7
60	930	11.2	6
1	1000	1.3	9
5	1000	4.1	4
15	1000	8.6	5
<u>Scaled</u>			
15	850	4.4	10
15	930	11.4	8
15	1000	27.3	12
<u>Commercial C-110M Titanium Alloy</u> (Initial hydrogen content, 55 ppm and 49 ppm, for scale-free and scaled samples, respectively)			
<u>Scale free</u>			
30	850	5.1	-5
60	850	8.3	-7
5	930	4.2	-8
15	930	7.2	-5
30	930	12	-6
60	930	15.5	+3
1	1000	1.7	0
5	1000	5.5	0
15	1000	13.5	+2
<u>Scaled</u>			
15	850	6.4	4
15	930	16.6	5
15	1000	27.7	6

TABLE 6. HYDROGEN PICKUP AND METAL LOSS FOR SODIUM HYDRIDE DESCALING^(a) OF A-55 AND C-110M TITANIUM-ALLOY 1/4-INCH ROD⁽⁷⁶⁾

Descaling Treatment Time, min	Temperature, F	Weight Loss, mg/cm ²	Hydrogen Absorption, ppm	Ratio of H ₂ Absorption (ppm) to Unit Weight Loss (mg/cm ²)
<u>Commercial Unalloyed A-55 Titanium</u> (Initial hydrogen content, 38 ppm)				
<u>Scale free</u>				
15	700	0.7	49	70
60	700	5.4	112	21
15	800	3.0	37	12
60	800	8.2	122	15
15	900	8.2	72	8.8
60	900	68	162	2.4
<u>Scaled</u>				
15	700	1.2	47	39
60	700	8.0	112	14
15	800	4.6	32	7.0
60	800	11.3	47	4.2
15	900	9.0	72	8.0
60	900	94.5	202	2.1
<u>Commercial C-110M (Ti-8Mn) Alloy</u> (Initial hydrogen content, 49 ppm)				
<u>Scale free</u>				
15	700	0.8	91	114
60	700	8.3	201	24
15	800	5.3	46	8.7
60	800	12.9	131	10
15	900	10	81	8.1
60	900	38	251	6.6
<u>Scaled</u>				
15	700	0.8	81	100
60	700	8.3	221	27
15	800	5.3	49	9.2
60	800	12.9	141	11
15	900	9.7	111	11
60	900	37.9	261	6.9

(a) Descaling bath contained 1.9 percent sodium hydride. The descaling treatment was followed by a brief dip in nitric-hydrofluoric acid bath for brightening.

hydride process, the time of immersion is generally the most important. If the material to be descaled is removed from the molten bath as soon as the oxide has been removed, contamination is virtually eliminated. This requires that the descaling time be altered as necessary with each new class of material processed.

A modified sodium hydride process has been reported in which the bath is saturated with titanium dioxide. (77) Although this bath reduces the metal loss and the amount of hydrogen absorbed by the material being descaled, the rate of scale removal is reported to be the same as that obtained with the unmodified sodium hydride process.

Acid pickling of titanium is used following chemical or mechanical descaling in many processing operations, to remove the layer of oxygen-contaminated metal beneath the scale. (75) In general, pickling solutions contain 2.4 percent hydrofluoric acid, 15-25 percent nitric acid, balance water, and are operated at 90 to 120 F. Alpha alloys or shapes having low surface-to-volume ratio are pickled occasionally in nitric-acid-free solutions. Removal of light contaminated layers with 5 to 10 percent sulfuric acid also has been reported. In acid pickling, the concentration of hydrogen atoms at the metal surface may reach an effective pressure of many atmospheres, so that absorption can occur with ease at the low temperatures involved. The hydrogen pickup in acid pickling can be eliminated by adding nitric acid in sufficient amounts.

In alpha alloys, the diffusion of hydrogen inward from the surface is quite slow, and a layer of hydride is formed on the metal surface by solutions which permit the liberation of atomic hydrogen. (72) Subsequent annealing permits this layer to diffuse into the part and, if the surface-to-volume ratio is high, severe bulk contamination may result. Diffusion is more rapid in alloys having a continuous beta phase, and bulk contamination of these alloys often occurs during pickling.

Secondary Fabrication and Hydrogen Contamination of Titanium. The principal sources of hydrogen contamination during secondary fabrication are solution heat treatment and acid pickling. The greater surface-to-volume ratio of material at this stage of fabrication increases the chances for hydrogen pickup considerably. Therefore, special precautions should be observed to prevent conditions favorable to contamination in final heat treatment and pickling.

It has been reported that some hydrogen contamination can occur during chemical milling; an increase in bulk hydrogen content of 150 to 200 ppm has been observed. However, immersion of the part in boiling water immediately after pickling reduced the contamination to 70 to 80 ppm.

Contamination During Service. Several failures of titanium parts have occurred that could be traced to hydrogen embrittlement resulting from contamination during service. In most cases contamination occurred because of failure to recognize that the environment in which titanium was placed contained a source of hydrogen of appreciable magnitude. If the use of titanium is contemplated in an environment known to contain hydrogen, particularly if the service temperature is above 500 F or if the hydrogen partial pressure is appreciable, testing should be conducted to insure that serious contamination will not occur during the service life of the part.

Hydrogen Embrittlement of Titanium Alloys

Characteristics of Hydrogen Embrittlement. Hydrogen in titanium is of concern primarily because, in sufficient concentrations, it can result in serious loss of ductility and/or the occurrence of delayed brittle failure. Hydrogen embrittlement in titanium and titanium alloys can be separated into two distinct types based upon the rate of load application; these have been designated impact embrittlement and low-strain-rate embrittlement.

Impact embrittlement is commonly observed in unalloyed titanium and in alpha alloys, the low-temperature hexagonal close-packed form of titanium. The loss of ductility results from the presence of a hydride phase in the alloy. (78) Impact embrittlement becomes more severe with increased hydrogen content, increased strain rate, decreased temperature, and the presence of notches in the part. As little as 150 ppm hydrogen can result in severe embrittlement of unalloyed titanium as measured in room-temperature impact tests. Although impact embrittlement is most troublesome in alpha alloys, a sufficiently high hydrogen content can result in impact embrittlement in beta alloys, (79) in which the high-temperature body-centered cubic form of titanium is stabilized to room temperature by alloying, and in alpha-beta alloys. However, the hydrogen content resulting in impact embrittlement in alpha-beta alloys is usually in excess of the amount that results in low-strain-rate embrittlement.

Low-strain-rate embrittlement is most frequently observed in hydrogen-contaminated alpha-beta alloys, but has also been reported in both alpha and beta alloys. (79,80) The effects of hydrogen content, strain rate, and temperature on the tensile ductility of a typical alpha-beta titanium alloy are shown in Figure 29. Of primary interest is the observation that embrittlement is absent at high strain rates, which is the principal basis for distinguishing between impact and low-strain-rate embrittlement.

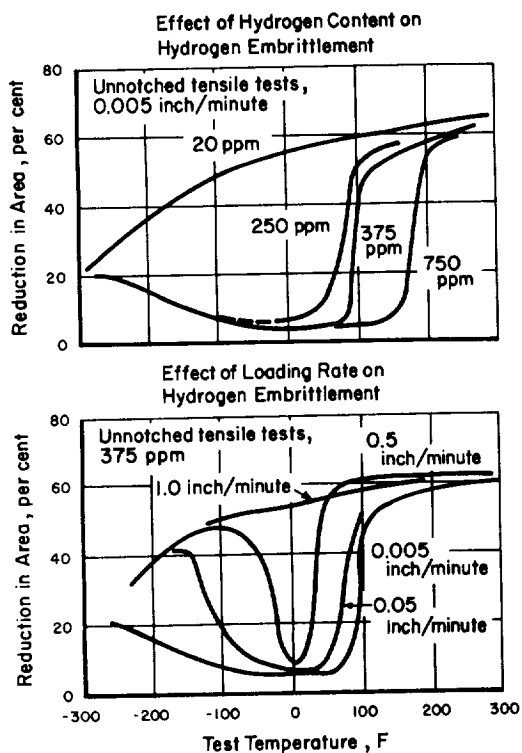


FIGURE 29. EFFECTS OF HYDROGEN CONTENT, STRAIN RATE, AND TEMPERATURE ON THE TENSILE DUCTILITY OF A TYPICAL α/β TITANIUM ALLOY⁽⁷⁸⁾

A-53059

The two types of hydrogen embrittlement appear to be quite closely related to each other, even though they produce distinctly different effects in titanium alloys. Both are believed to result from a decrease in solubility of hydrogen in titanium alloys with decreasing temperatures. The difference in behavior can be related to differences in the kinetics of hydride precipitation.

The correlation between brittleness in impact loading and the presence of a hydride phase in alpha titanium alloys is well documented.⁽⁶²⁾ It is probable that the presence of titanium hydride acts in two ways: (a) through its ability to act as a stress raiser in the alloy and (b) through its inherent brittleness which results in the introduction of numerous microcracks. Since the hydride phase is randomly located, brittleness is observed only when conditions are such that ductile behavior of the matrix is minimized, that is, at high strain rates, low temperatures, or in the presence of a severe external notch.

The presence of hydride near the fracture region in alloys that have failed by low-strain-rate embrittlement has occasionally been reported. However, more frequently no hydride is found at the fracture, and this observation has been interpreted to indicate that embrittlement is not directly related to the presence of hydride.⁽⁸⁰⁾ The hydride phase in hydrogen-containing alpha-beta titanium alloys occurs in a highly localized manner, preferentially in the alpha-beta interfacial region. Hydride precipitation under stress apparently occurs preferentially on a plane perpendicular to the principal applied stress. If the stress is high enough, cracking may occur along the hydride phase. The correlation between the location of hydride when it is observed in alpha-beta alloys and the fracture path in alloys showing low-strain-rate embrittlement suggests that brittleness is a direct result of hydride precipitation. Failure to locate hydride in the fracture region, particularly in notched samples, is not conclusive evidence that none was present, since the hydride tends to be highly localized and may induce failure when present in small amounts.

Very little information on the embrittlement behavior of all-beta alloys is available. What is available,^(80,81) can be interpreted to show either general embrittlement at quite high hydrogen contents or low-strain-rate embrittlement closely followed by impact embrittlement. Since no hydride has been observed to form in all-beta alloys (not even when they are brittle under impact loading), the former explanation is favored.

Discussion of embrittlement data will be limited to those pertaining to the Ti-6Al-4V alloy, since it is the only titanium alloy under investigation in the present program. Ti-6Al-4V is an age-hardenable, alpha-beta alloy. With 6 percent aluminum, this alloy should be one of the most insensitive to hydrogen embrittlement of the alpha-beta alloys because of the effects of aluminum in retarding hydrogen absorption, as was discussed previously. Embrittlement is generally not observed until quite large amounts of hydrogen are present. For example, stabilized material has been found to be capable of containing 800 ppm without adverse effects.⁽⁸²⁾ On the other hand, samples of coarse-grained, acicular material in the aged condition have exhibited embrittlement with 300 ppm hydrogen, and material in the stabilized condition was found to be embrittled by only 200 ppm when given a pretreatment to produce a very coarse alpha grain size with a continuous beta network separating the alpha grains.⁽⁶³⁾ However, these were exceptional cases, not likely to be encountered in commercial sheet. It has been reported that hydrogen contents up to 150 ppm do not adversely affect the properties of welded joints in Ti-6Al-4V.⁽⁸³⁾

Riesen and Kah⁽⁸⁴⁾ showed that Ti-6Al-4V showed no significant embrittlement effects at hydrogen contents up to 240 ppm. However, at 294 ppm hydrogen, significant embrittlement was indicated.

Hydrogen Embrittlement of Ti-6Al-4V Resulting From Processing Operations. Very few data exist on the hydrogen embrittlement of titanium alloys in general as a result of hydrogen introduced by normal processing operations. As was pointed out earlier, those processes which could introduce damaging amounts of hydrogen have been recognized and by careful control the danger of embrittlement has been minimized.

Electrodeposited coatings of chromium have been considered for obtaining a wear-resistant surface on titanium. However, the adhesion of chromium plate to titanium is not comparable to that obtained on steel. The key to adherent plate appears to lie in the preparation and delivery of an oxide-free surface to the plating bath. Electroless nickel plating has been used chiefly for corrosion protection. However, in some cases electroless nickel has been used where resistance to wear, abrasion, and galling was of prime importance. DMIC Memorandum No. 35⁽⁸⁵⁾ reprinted in March, 1965, gives the details on various procedures for plating on titanium based on 21 selected references.

Schlosser and Lowery,⁽⁸⁶⁾ in a report on the development of a procedure for electroplating on Ti-6Al-4V to protect it from reaction with liquid oxygen, found no evidence of hydrogen embrittlement of the alloy as a result of electroplating with copper, nickel, or chromium or applying electroless nickel coatings. However, these investigators did report a significant loss in ductility of the Ti-6Al-4V alloy as a result of pickling in sulfuric acid.

Hydrogen Removal From Titanium

Hydrogen removal from titanium alloys is accomplished effectively only by vacuum annealing at rather high temperatures. Hydrogen removal is conducted at the maximum temperature that does not adversely affect the properties of the alloy and at the minimum hydrogen partial pressure available in the equipment being used. Prevention of undesirable changes in properties generally limits the maximum temperature used to 1200-1500 F. For the Ti-6Al-4V alloy, this temperature is $1500\text{ F} \pm 35\text{ F}$. The time required to vacuum anneal hydrogen-containing material is a function of the rate at which hydrogen can diffuse out of the material and the rate of removal of hydrogen gas from the vicinity of the sample.

Commercial degassing operations are carried out under a wide variety of conditions. Two procedures reported involve vacuum annealing as follows:

- (1) 3 to 36 hours at 1250 to 1800 F, 1 micron total pressure⁽⁸⁷⁾
- (2) 8 to 72 hours at 1200 to 1500 F, maximum total pressure of 0.1 micron.⁽⁷⁵⁾

Degassing may lead to dimensional changes that are objectionable in close-tolerance finish-machined parts. A measurable volume contraction occurs in titanium upon the removal of hydrogen. However, dimensional changes in finish-machined parts

during vacuum annealing generally have been traced to the relief of residual stress, rather than hydrogen removal.

Hydrogen-Embrittlement Relief Treatments

If hydrogen-induced, delayed brittle failures of high-strength metallic parts are to be prevented, hydrogen must be eliminated from the parts. The ideal way to solve this problem is to prevent hydrogen from entering the parts during all processing operations. However, in many cases this approach is not practicable; therefore, hydrogen which is unavoidably picked up during processing must be removed or put into a nondamaging form. The most common procedure for removing hydrogen is to bake it out.

The early investigations of hydrogen embrittlement induced by pickling in acid solutions or by electrolysis showed that aging at room temperature or heating to moderately elevated temperatures causes a gradual recovery of the original ductility. Some investigators reported that complete recovery had been obtained, while others found that recovery was incomplete at either room temperature or at elevated temperatures. However, this early work was done largely with low-carbon steel.

Apparently, low-alloy steels, heat treated to high strength levels, completely recover the ductility lost by hydrogen introduced during acid pickling if they are stored for a long time before use, or if they are baked at a sufficiently high temperature, provided that they are not electroplated after pickling. For example, tensile tests of SAE 4340 steel, heat treated to a hardness of Rockwell C 47, indicated that complete recovery of the ductility lost as a result of pickling in hydrochloric acid for 1 hour was accomplished by aging at room temperature for 5 hours or more. (88)

Bastien⁽⁸⁹⁾ studied the influence of the environment on the recovery of the bend characteristics of steel specimens embrittled by pickling in hydrochloric acid. He found that a markedly faster rate of recovery was achieved when the specimens were immersed in water or were in air saturated with water vapor, than when they were in dry air. Other investigators^(90,91) have reported that immersion in hot water is more effective in removing hydrogen from steel than is exposure to hot air at the same temperature. Of course, both are considerably more effective than storage in air at room temperature. Also, additional reports of a qualitative nature have indicated that hydrogen removal is more rapid in water than in air. Probert and Rollinson⁽⁹²⁾ showed that embrittlement induced by hydrogen introduced during cathodic cleaning or acid pickling was easily relieved by heating the steel at moderate temperatures for relatively short periods of time. Their results are summarized in Figure 30. They also showed that hydrogen absorbed during treatments prior to electrolytic or electrodeless nickel plating was partially removed during the plating operations themselves, presumably because the elevated temperatures of the solution caused some outgassing of hydrogen.

In addition to the undesirable effects that occur when hydrogen is codeposited with a desired metal electroplate (reduction in ductility and susceptibility to hydrogen-stress cracking), the plate has another effect. The presence of a more-or-less impermeable metal coating, such as cadmium, makes the evolution of hydrogen from the interior of the base metal more difficult; this may serve to aggravate the effects of embrittlement and delayed failure of electroplated steel. Although an appropriate

baking treatment may restore most or all of the ductility to the plated steel, often such a treatment does not overcome the propensity toward hydrogen-stress cracking, as has already been shown in the section on embrittlement resulting from electroplating.

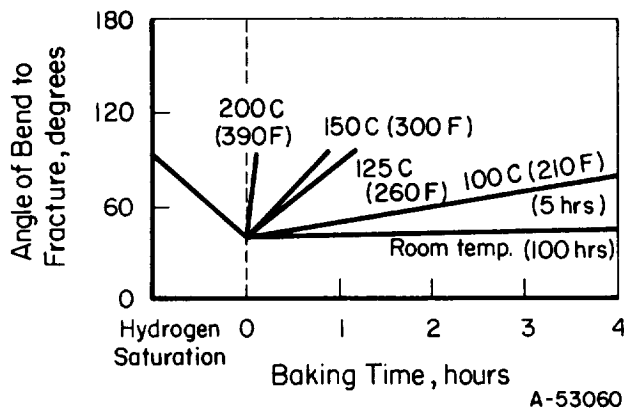


FIGURE 30. REMOVAL OF HYDROGEN EMBRITTLEMENT IN A TOOL STEEL OF HIGH CARBON CONTENT AFTER PICKLING OR CATHODIC CLEANING BUT WITHOUT ELECTROPLATING⁽⁹²⁾

There are very few specifications pertaining to hydrogen embrittlement and methods of alleviating it. However, in view of the complexity of the problem of hydrogen embrittlement, it is not surprising that the specifications are few in number and vague in character. There is nothing in those specifications and recommended practices of ASTM pertaining to metal finishing that has to do with processes that are nonembrittling for use in situations where embrittlement is commonly encountered. In specifications for zinc plating and for cadmium plating on steel, the only provision is that, after all metal-finishing operations are completed, the steel must be free from the detrimental effects of hydrogen embrittlement. It is further provided that the manufacturer and purchaser shall agree upon test methods and techniques of evaluation for freedom from hydrogen embrittlement. A note in each of the passages in the zinc and cadmium specifications cautions that hardened steels and cold-worked steels are particularly susceptible to damage and that careful control of cleaning and plating is needed to minimize hydrogen embrittlement. The note warns also that baking should be employed to remove embrittlement that unavoidably may be present after a finishing operation.

Most of the Federal specifications for metal finishes have a provision to the effect that all steel parts having a hardness greater than Rockwell C 40 must be stress relieved prior to plating if they contain objectionable residual stresses. None of the Federal specifications prescribe procedures that will prevent hydrogen embrittlement, but those for cadmium, chromium, nickel, silver, and zinc plating contain directions for baking some kinds of work pieces. The specifications are prescribed for parts that are to be flexed or repeatedly loaded by impact. This seems to neglect the many instances of failure that can occur from steady, uniform loading at stresses below the yield point.

In selecting a baking treatment to relieve hydrogen embrittlement, several factors must be considered. The baking temperature must not be such as to reduce the mechanical properties of the part. For cadmium plates, temperatures over 400 F can produce discoloration of the plate. Temperatures above 610 F, the melting point of cadmium, must be avoided because liquid cadmium can cause embrittlement of steel. Under many conditions, cadmium embrittlement of steel can occur at temperatures appreciably below the melting point of pure cadmium.

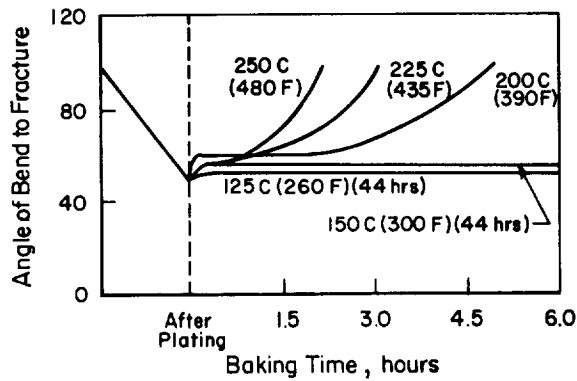
Before steel strength levels were raised to the point where delayed brittle failures were encountered, the most common relief practice for hydrogen embrittlement resulting from cadmium plating consisted of baking at 375 to 400 F for 3 or 4 hours. When hydrogen-stress cracking was encountered, baking times often were increased to 23 hours, but this practice was only partially effective in alleviating the susceptibility to hydrogen cracking. Baking at 375 F for 23 hours is the most common hydrogen relief treatment employed today.

Two factors which greatly influence the recovery of properties by baking cadmium-plated specimens are the plate thickness and plate porosity. Chek⁽⁹³⁾ investigated the influence exerted by variation in thickness of cadmium plate deposited from a cyanide bath upon recovery from hydrogen embrittlement of AISI 4340 steel (270,000-psi strength level) by baking at 300 F for periods up to 24 hours. Two procedures were used for the detection and evaluation of hydrogen embrittlement - tensile tests of unnotched specimens and the sustained-load test using notched specimens. Recovery, as indicated by the restoration of original ductility in a tensile test, was attained at baking times of 4 hours or less when the plate thickness ranged from 0.5×10^{-4} to 1.25×10^{-4} inch; but recovery was not attained at commercial thicknesses of 2.5×10^{-4} inch or more. Under sustained loading, however, hydrogen-stress cracking occurred in spite of the baking treatment when the plating thickness exceeded 0.5×10^{-4} inch.

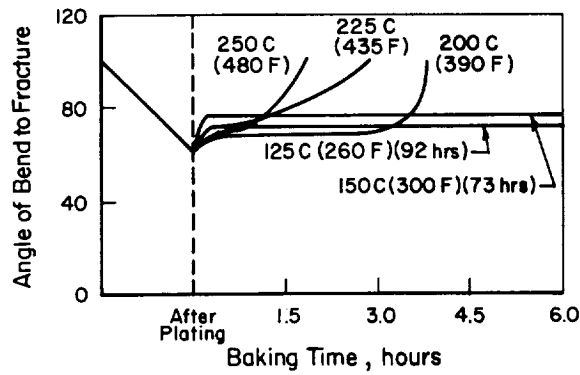
Probert and Rollinson⁽⁹⁴⁾ evaluated the effects of various baking treatments on the relief of hydrogen embrittlement induced in a high-strength tool steel of high carbon content by cadmium plating; they used a bend test and the criterion for recovery was recovery of bend angle at fracture. Their results are shown in Figure 31. Preliminary investigations at temperatures of 125 C (260 F) and 150 C (300 F) showed no evidence of recovery with soak times varying between 44 and 92 hours. Further work showed that temperatures exceeding 190 C (375 F) were required to effect complete recovery.

As was pointed out previously, cadmium-plating baths without brighteners produce plates of greater porosity than do similar baths that contain brighteners; such porous plates facilitate the removal of hydrogen during baking treatments. The work of Geyer, et al⁽⁴⁴⁾, showed, however, that some specimens of AISI 4340 steel (290,000-psi strength level) plated from fluoborate baths with various additions to improve the quality of the plate failed during sustained load tests after being baked at 375 F for 23 hours. Specimens plated in a high-efficiency cyanide bath without brightener did not fail in the sustained load test after being baked for 23 hours at 375 F. However when a brightener was added to improve the quality of the deposit, a plated-and-baked specimen failed after only 33 hours. This was attributed to the bright electroplate being more dense and, hence, providing a barrier to hydrogen removal during baking.

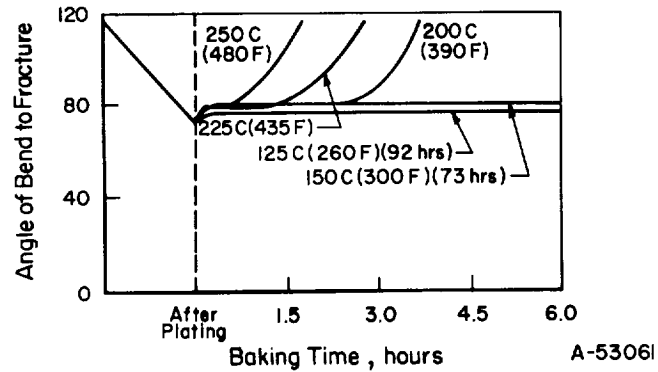
Glorioso⁽⁹⁵⁾ studied the embrittlement relief of AISI 4340 steel heat treated to strength ranges of 200,000 to 220,000 psi and 260,000 to 280,000 psi and AISI Type H-11 steel at the 250,000 to 280,000-psi strength level from an electroless nickel plating bath. The notched specimens were anodic alkaline cleaned, given a Wood's nickel strike, and then electroless nickel plated to a plate thickness of 0.0010 to 0.0015 inch. The SAE 4340 specimens at the 200,000 to 220,000-psi strength level were baked 8 hours at 375 F, while the SAE 4340 steel specimens at the 260,000 to 280,000-psi strength level were baked 23 hours at 375 F; the H-11 steel samples were



(a) Hardened but not tempered; Vickers Hardness = 535



(b) Tempered at 420 C (790 F); Vickers Hardness = 420



(c) Tempered at 460 C (860 F); Vickers Hardness = 340

FIGURE 31. REMOVAL OF HYDROGEN BY BAKING AFTER CADMIUM PLATING OF STEELS AT DIFFERENT HARDNESS LEVELS⁽⁹⁴⁾

Tool steel for feeler gages (C = 1.0 to 1.8%).
 Plate thickness = 0.00045 inch.

baked 1 hour at 600 F. No failures were obtained from any of the specimens loaded to 75 percent of their notched tensile strength for 200 hours.

The recovery of embrittlement from chromium electroplates is an excellent example of the effect of plate porosity. Even though high-strength steels have been shown to be more severely embrittled by chromium plating than by cadmium plating,⁽⁵⁰⁾ embrittlement relief is more easily achieved during baking treatments in the case of the chromium-plated steels, presumably because the chromium plate is more porous. Krieg⁽⁵³⁾ showed that no chromium-plated, notched tensile specimens of AISI 4340 steel (220,000 to 240,000-psi strength range) survived more than 5 hours under a sustained load of 75 percent of their notched tensile strength when they were not baked after being plated. However, all of the specimens which received a 23-hour bake at 375 F before loading survived 100 hours at stresses of 75 percent and 90 percent of their notched tensile strengths.

Probert and Rollinson⁽⁹⁶⁾ also showed that the barrier effect of chromium plates that ranged in thickness from 0.00025 inch to 0.00050 inch was of a lower order than that for either copper or cadmium deposits of comparable thickness. Complete relief of embrittlement of chromium-plated parts was obtained in less than 5 hours at 100 C (212 F). The lower barrier effect of chromium to the removal of hydrogen during relief treatments was considered to result from the grain size and the natural crack pattern of deposits in the high-hardness range. It was found that, on increasing the thickness of chromium above 0.0005 inch, to effect satisfactory relief from embrittlement it was necessary to increase heat-treatment times and temperatures, but at no time was it found necessary to exceed the time-temperature conditions established for copper and cadmium deposits. The results of their studies are shown in Figure 32.

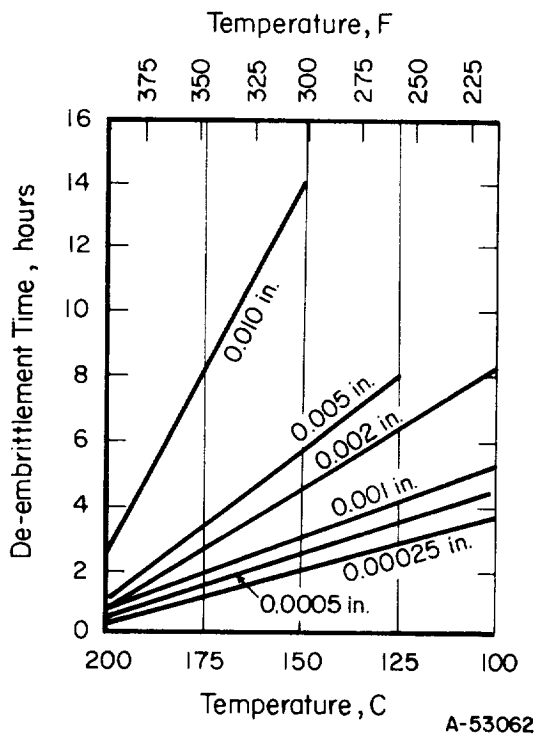


FIGURE 32. HYDROGEN-EMBRITPLEMENT RECOVERY TIMES AND TEMPERATURES FOR DIFFERENT THICKNESSES OF ELECTRODEPOSITED CHROMIUM (STANDARD BATH)⁽⁹⁶⁾

The strength level of an electroplated part also influences the effectiveness of embrittlement-relief treatments. As was shown in the section on electroplating, lost ductility generally can be recovered in steels with lower strength levels by short baking times at a given temperature, but ductility may not be completely recovered in higher strength steels after considerably longer baking times at the same temperature. This behavior seems to be closely related to the susceptibility of the material to embrittlement, that is, recovery is more easily achieved in the less susceptible materials. This effect is shown by the plating processes used by one manufacturer for cadmium coating high-strength steel fasteners, as shown in Table 7.⁽⁹⁷⁾

TABLE 7. CADMIUM-COATING PROCESSES USED ON HIGH-STRENGTH STEEL AIRCRAFT FASTENERS⁽⁹⁷⁾

Tensile Strength of Fastener	Less than 180,000 psi	180,000 to 250,000 psi	250,000 psi and higher
Specification	QQ-P-416	NAS 672	MIL-C-8837
Plating Procedure	Cyanide	Fluoborate	Vacuum
Baking Practice	3 hours at 375 F	23 hours at 375 F	None

AISI Type H-11 steel and the 18Ni maraging steels, which have been shown to be less susceptible to hydrogen embrittlement resulting from electroplating, appear to recover from the effects of hydrogen easier than AISI 4340 steel during postplating relief treatments. Baking nickel/chromium-plated 18Ni maraging steel at 450 F for 24 hours effectively prevented delayed failure at 90 percent of the notched tensile strength.⁽⁵⁵⁾ Specimens that were not baked failed on loading to 81 percent of their notched tensile strength. Figure 33 shows the effect of baking for various times at 300 F on the recovery of mechanical properties of cathodically charged 18Ni maraging steel.⁽⁹⁸⁾ According to Reference (98), a bake of 24 hours at 400 to 600 F is usually sufficient to recover the full mechanical properties of the 18Ni maraging steel.

The results of the various investigations on the effectiveness of various hydrogen-embrittlement relief treatments indicate that many variables influence the effectiveness of these treatments. These variables include steel composition, the strength level of the steel, the applied stress level, the test method used, the presence of a coating, and the structure and thickness of the coating.

The results show that hydrogen is more easily removed when no coating is present. When the section size is not too great, baking at 375 for 1 to 5 hours appears to restore the properties to high-strength steels that have been pickled or cathodically charged. However, when a coating is present, longer baking times are necessary. Thin electroplates and porous electroplates facilitate hydrogen removal, while thicker plates and dense plates hinder hydrogen removal during baking treatments. Also, steels of lower strength level (below 180,000 psi) have been shown to be nearly completely relieved of the effects of hydrogen by baking treatments. However, the higher strength steels have shown a propensity toward hydrogen-stress cracking even after longer baking treatments.

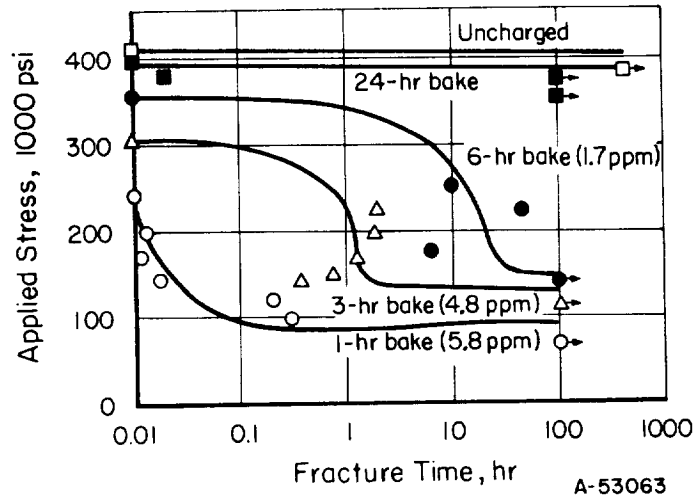


FIGURE 33. HYDROGENATED 18% Ni MARAGING STEEL RAPIDLY REGAINS RESISTANCE TO HYDROGEN-STRESS CRACKING WHEN BAKED AT 300 F⁽⁹⁸⁾

Hydrogenation: 0.07 amp per sq. in. for 21 hours.

Investigators have shown that the ductility of a steel part as measured in a conventional tensile test may be completely restored by a baking treatment, but the steel may still be susceptible to hydrogen-stress cracking. Therefore, only when the various variables are fixed can a relief process be said to be effective, and only for those fixed conditions.

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