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NASA TM X- 68088

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HYDROGEN ENVIRONMENT EMBRITTLEMENT

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TECHNICAL PAPER proposed for presentation at
Standardization of Test Methods for Hydrogen Embrittlement
sponsored by the American Society for Testing and Materials
Los Angeles, California, June 26, 1972

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ABSTRACT

Hydrogen embrittlement is classified into three types: internal reversible hydrogen embrittlement, hydrogen reaction embrittlement, and hydrogen environment embrittlement. Characteristics of and materials embrittled by these types of hydrogen embrittlement are discussed. Hydrogen environment embrittlement is reviewed in detail. Factors involved in standardizing test methods for detecting the occurrence of and evaluating the severity of hydrogen environment embrittlement are considered. The effects of test technique, hydrogen pressure, purity, strain rate, stress concentration factor, and test temperature are discussed. Additional research is required to determine whether hydrogen environment embrittlement and internal reversible hydrogen embrittlement are similar or distinct types of embrittlement.

KEY WORDS: hydrogen environment embrittlement, internal reversible hydrogen embrittlement, hydrogen reaction embrittlement.

INTRODUCTION

Hydrogen embrittlement of metals is an old, a frequently encountered, and often misunderstood phenomenon. Metals processing, chemical and petrochemical industries have experienced various types of hydrogen problems for many years. More recently, however, the aerospace industry has experienced new and unexpected hydrogen embrittlement problems.

There are many sources of hydrogen, several types of embrittlement, and various theories for explaining the observed effects   Before reviewing the subject of hydrogen environment embrittlement, we must first classify and briefly discuss all the types and characteristics of hydrogen embrittlement.

For purposes of this discussion, hydrogen embrittlement will be classified into three types:

1. Internal reversible hydrogen embrittlement

2. Hydrogen reaction embrittlement

3. Hydrogen environment embrittlement

The definitions of these three types of embrittlement are as follows. If specimens have been <u>precharged</u> with hydrogen from any source or in any manner and embrittlement is observed during mechanical testing, then embrittlement is due to either internal reversible embrittlement or to hydrogen reaction embrittlement. If hydrides or other new phases containing hydrogen form during testing in gaseous hydrogen, then for the purpose of this paper, embrittlement will be attributed to hydrogen reaction embrittlement. For all embrittlement determined during mechanical testing in gaseous hydrogen other than internal reversible and hydrogen reaction embrittlement, hydrogen environment embrittlement is assumed to be responsible.

<u>Internal reversible hydrogen embrittlement</u>. - Internal reversible hydrogen embrittlement has also been termed slow strain rate embrittlement or delayed failure. This is the classical type of hydrogen embrittlement that has been studied quite extensively. Widespread attention has

been focused on the problem resulting from electroplating - particularly of cadmium on high strength steel components. Other sources of hydrogen are processing treatments, such as melting and pickling. More recently, the embrittling effects of many stress-corrosion processes have been attributed to corrosion-produced hydrogen. Hydrogen that is absorbed from any source is diffusable within the metal lattice. To be fully reversible embrittlement must occur without the hydrogen undergoing any type of chemical reaction after it has been absorbed within the lattice.

Internal reversible hydrogen embrittlement can occur after a very small average concentration of hydrogen has been absorbed from the environment. However, local concentrations of hydrogen are substantially greater than average bulk values. For steels, embrittlement is usually most severe at room temperature during either delayed failure (static fatigue) or slow strain rate tensile testing. This time-dependent nature (incubation period) of embrittlement indicates that diffusion of hydrogen within the lattice controls this type of embrittlement. Cracks initiate internally, usually below the root of a notch at the region of maximum triaxiality. Embrittlement in steel is reversible (ductility can be restored) by relieving the applied stress and aging at room temperature, provided microscopic cracks have not yet initiated. Internal reversible hydrogen embrittlement has also been observed in a wide variety of other materials including nickel-base alloys and austenitic stainless steels provided they are severely charged with hydrogen.

Hydrogen reaction embrittlement. - Although the sources of hydrogen may be any of those mentioned previously, this type of embrittlement is

quite distinct from that discussed in the previous section. Once hydrogen
is absorbed into the lattice, it may react near the surface or diffuse sub-
stantial distances before it reacts. Hydrogen can react with itself, with
the matrix, or with a foreign element in the matrix. The chemical reactions
that comprise this type of embrittlement or attack are well known and are
frequently encountered. The new phases formed by these reactions are
usually quite stable and embrittlement is not reversible during room tem-
perature aging treatments.

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

Hydrogen environment embrittlement. - Hydrogen environment embrittle-
ment was recognized as a serious problem in the mid 1960's when NASA and
its contractors experienced failures of ground based hydrogen storage tanks
(Refs. 1 and 2). These tanks were rated for hydrogen at pressures of
35 to 70 MN/m^2 (5000 to 10 000 psi). Consequently, the failures were attrib-
uted to "high pressure hydrogen embrittlement." Because of these failures
and the anticipated use of hydrogen in advanced rocket and gas-turbine

engines and auxiliary power units, NASA has initiated both in-house (Refs. 3 through 5) and contractural (Refs. 6 through 14) research. The thrust of the contractural effort generally has been to define the relative susceptibility of structural alloys to hydrogen environment embrittlement. A substantial amount of research has been concerned with the mechanism of the embrittlement process (Refs. 4, 5, 15 through 25). There is marked disagreement as to whether hydrogen environment embrittlement is a form of internal reversible hydrogen embrittlemet or is truly a distinct type of embrittlement. Some background information regarding this controversy will be presented in this paper. These controversial aspects will be considered in detail later in this Symposium.

This paper is exclusively concerned with this more recently encountered form of hydrogen embrittlement - hydrogen environment embrittlement. The purpose of this paper is to review the factors in hydrogen environment embrittlement which must be considered in any effort to standardize test methods for detecting and evaluating this type of embrittlement. To do this, we must examine the characteristics of hydrogen environment embrittlement as well as the similarities and dissimilarities between hydrogen environment embittlement and both internal reversible embrittlement and hydrogen reaction embrittlement. The effect of various experimental variables such as gas pressure, gas purity, test strain rate, stress concentration factor, and test temperature on hydrogen environment embrittlement will be discussed. The relative sensitivity of the tensile, fatigue, creep, fracture toughness, and disc pressure tests used by investigators will also be discussed. This paper will attempt to set the stage for subsequent

papers in this Symposium which will present detailed descriptions of test specimens and test procedures for evaluating hydrogen environment embrittlement of materials.

REVIEW OF HYDROGEN ENVIRONMENT EMBRITTLEMENT

Characteristics of Hydrogen Environment Embrittlement

Hydrogen environment embrittlement may occur when an essentially hydrogen-free material is mechanically tested in gaseous hydrogen. It is well agreed among investigators that molecular hydrogen must dissociate to atomic hydrogen for embrittlement to occur. The physical and chemical steps necessary for hydrogen environment embrittlement, as well as the other types of hydrogen embrittlement, are illustrated in Figure 1. For hydrogen environment embrittlement to occur, both adsorption (physisorption, dissociation, and chemisorption) and absorption probably take place (steps 1 through 5). The necessity for subsequent lattice diffusion (step 5 to 6) for hydrogen environment embrittlement has provoked marked disagreement. If it is eventually shown that hydrogen must diffuse through the lattice for embrittlement to occur during testing in gaseous hydrogen, hydrogen environment embrittlement may then be considered equivalent to internal reversible hydrogen embrittlement.

The characteristics of hydrogen environment embrittlement are listed in Table I. Hydrogen environment embrittlement has been observed over a wide range of gas pressures, temperatures, and in a variety of mechanical tests. Embrittlement appears to be most severe near room temperature. Gas purity and test strain rate can play significant roles in determining the degree of embrittlement. As will be discussed subsequently, the trans-

fer step of surface adsorption has been shown to be the overall rate controlling step during hydrogen environment embrittlement (Refs. 4 and 5). However, if adsorption is bypassed, the rate controlling step for hydrogen environment embrittlement is either absorption (Refs. 5 and 23) or subsequent lattice diffusion (Refs. 15, 18, and 24). Analyses of substantial increases in the hydrogen content (Refs. 20, 22, and 24) of embrittled alloys tend to support the necessity for lattice diffusion since it is unlikely that such large quantities of hydrogen can be absorbed within the first atomic layer below the surface. Another important characteristic of hydrogen environment embrittlement that has not been conclusively resolved in the location of crack initiation - at the surface (Ref. 23) or internally (Refs. 15, 18 and 20). These characteristics can be compared with those observed for internal reversible hydrogen embrittlement and for hydrogen reaction embrittlement which are also listed in Table I.

Hydrogen environment embrittlement has been observed in a wide variety of materials. The high strength structural alloys such as steels and nickel-base alloys are particularly susceptible. Metals and alloys subject to all types of hydrogen embrittlement are listed in Table II. Those affected by hydrogen environment embrittlement (Refs. 14 and 23) and internal reversible hydrogen embrittlement (Ref. 26) are listed in the approximate order of decreasing susceptibility at room temperature. The metals affected by hydrogen reaction embrittlement are also listed in Table II and the types of reactions are called out.

It is important to note that nickel alloys are very susceptible to hydrogen environment embrittlement while they are relatively unsusceptible to

internal reversible hydrogen embrittlement. This difference in sensitivity may be related to some undefined surface characteristic of nickel alloys. This marked difference is susceptibility exhibited by nickel alloys has been responsible for some of the controversy as to whether the mechanism of hydrogen environment embrittlement is the same as the mechanism for internal reversible hydrogen embrittlement. With this one major exception, the relative susceptibility of most classes of materials to both these types of embrittlement is remarkably similar.

Severity of embrittlement has also been observed to vary with both alloy form and annealing temperature. The degradation of notched tensile properties of Inconel 718 in bar, forging, and plate forms and in two solution annealed conditions is shown in Table III (Ref. 9). For example, bar and forgings annealed at the lower temperature are more severely embrittled than the same forms annealed at the higher temperature. For plate, the reverse ranking holds. These effects have been attributed to as-received and heat-treated precipitate (Ni_3Nb) morphology (Ref. 9) and grain size (Refs. 9 and 10). The least embrittled structure is one which is fine grained with a uniform dispersion of the precipitate. The most embrittled structure is one which is large grained with intergranular precipitates.

Although these microstructural effects may be valid for Inconel 718, other severely embrittled nickel-base alloys (Refs. 12 to 14) do not contain niobium (Udimet 700, Rene 41, and Hastelloy X). In fact, Nickel 270 does not contain any elements that are likely to form precipitates. Hence, it is unlikely that hydrogen environment embrittlement can be attributed exclusively to precipitated phases. The role of grain size and grain boundaries

is also unresolved, particularly in light of the severe degree of hydrogen environment embrittlement recently reported for directionally solidified MAR M-200 (Ref. 13).

Effect of Test Variables

Hydrogen gas pressure. - Most of the materials listed in Table II were tested in a single investigation (Refs. 14 and 23) at a hydrogen pressure of 70 MN/m^2 (10 000 psi) at room temperature. Notched tensile strength and both smooth and notched reduction of area were used as the embrittlement criteria. Subsequent research (Refs. 11 and 14) indicated that embrittlement can occur in hydrogen at much lower gas pressures. For example, tensile properties of A302-B steel and Inconel 718 determined over a range of hydrogen pressures from 0.7 to 70 MN/m^2 (100 to 10 000 psi) are compared with tensile properties in helium in Figure 2. These investigators suggested that the degree of embrittlement was proportional to the square root of the hydrogen gas pressure.

More recent investigations (Refs. 4 and 25) have demonstrated that hydrogen environment embrittlement occurs at gas pressure substantially below atmospheric pressure. Fatigue crack growth rates of Nickel 200 at room temperature increased by an order of magnitude over the pressure range 1 uN/m^2 to 20 kN/m^2 (10^{-8} to 150 torr) (Ref. 25). The threshold stress intensity factor (K_{TH}) required for the initiation of measurable slow crack growth in 4130 steel in air decreased substantially in hydrogen at very low pressures (Refs. 4 and 5). For example, embrittlement was detected in molecular hydrogen at pressures of 17 kN/m^2 (127 torr), Figure 3(a), and in an atomic-molecular hydrogen mixture at a gas pressure of 1 N/m^2

$(8\times10^{-3}$ torr), Figure 3(b). As evident from the data presented in Figure 3, embrittlement was a function of both test crosshead speed and test temperature. The significance of testing speed, testing temperature, and gas composition will be discussed in subsequent sections of this paper.

These same investigators (Ref. 4) have also demonstrated that the degree of embrittlement is proportional to the square root of the gas pressure. However, they showed that such a relation is true only in a relatively narrow temperature range near room temperature. They proposed that the transfer step of surface adsorption of hydrogen was the overall rate controlling step in the process of hydrogen environment embrittlement.

Hydrogen gas composition. - The influence of gas purity is dramatically illustrated by the crack extension data shown in Figure 4. Crack extension in a stressed precracked sheet specimen of H-11 steel could be started by the introduction of pure hydrogen, and a running crack could literally be stopped by the introduction of oxygen-doped hydrogen (Ref. 17). These investigators reported that crack propagation rates were not affected by an atmosphere of hydrogen containing less than 200 ppm oxygen at a total gas pressure of 0.1 MN/m^2 (15 psi). However, at higher gas pressures, even lower concentrations of oxygen impurities inhibit embrittlement in gaseous hydrogen (Refs. 16 and 17). This inhibiting effect of oxygen is probably related to the preferential adsorption of the oxygen at freshly generated crack tips (Ref. 17).

It is interesting to note that hydrogen environment embrittlement is not eliminated by dilution of hydrogen with inert gases. For example,

measurable reductions of notched tensile properties were reported for both steels and nickel-base alloys for tests conducted in 70 MN/m^2 (10 000 psi) helium containing only 44 ppm hydrogen (Ref. 14).

Some recently reported crack growth tests were conducted in an atomic-molecular hydrogen mixture achieved by a clever experimental procedure (Ref. 5). An atomic-molecular hydrogen gas mixutre was created near the crack tip by dissociating molecular hydrogen on a hot filament. At a gas pressure of only 1 N/m^2 (8×10^{-3} torr), crack growth rates were several orders of magnitude greater in the atomic-molecular mixture than predicted rates in molecular hydrogen (Ref. 4). As shown in Figure 3(b), crack growth persisted to the limit of their experimental temperature capability (164° C), whereas, crack growth diminished in molecular hydrogen as the test temperature was raised above room temperature. These test results confirmed that hydrogen adsorption is a transfer step which is the overall rate controlling step in the process of hydrogen environment embrittlement. When this slow reaction step is bypassed by creating atomic hydrogen near the crack tip, then the rate controlling step for embrittlement is either absorption of hydrogen into solution or lattice diffusion of hydrogen.

These results also suggest that, if sufficient atomic hydrogen were available, embrittlement might occur to a greater degree and over a broader range of temperatures and pressures than determined in laboratory tests to date. Such a phenomena is particularly significant in regard to advanced engine applications that may use hydrazine or other fuels which decompose to atomic hydrogen.

The effect of an environment of water saturated hydrogen on the tensile properties of Udimet 700 has also been determined (Ref. 12). All tensile

properties over the temperature range 150° to 305° C were essentially identical to those determined in dry hydrogen, as will be shown later in the section on the effect of test temperature. These results are not consistent with the crack growth inhibiting effects reported for both wet hydrogen (Ref. 21) and oxygen plus hydrogen (Fig. 4). It is possible that contaminants in hydrogen readily inhibit embrittlement when testing precracked specimens, while the gross plastic deformation which occurs when testing smooth tensile specimens may negate such an inhibiting effect.

Test strain rate. - Some of the initial investigations of hydrogen environment embrittlement were concerned with the influence of test strain rate (Refs. 16 and 22). These tests demonstrated that embrittlement was more severe at low strain rates than at high strain rates. Such strain rate sensitivity is a well known characteristic of internal reversible hydrogen embrittlement and implies that hydrogen diffusion through the metal lattice during mechanical testing controls the degree of embrittlement. An identical effect may be occurring during hydrogen environment embrittlement or it is possible that the observed strain rate sensitivity is simply a manifestation of the time that freshly created surfaces are exposed to hydrogen.

The more recent experimental investigations have been concerned with screening numerous materials for relative susceptibility to hydrogen environment embrittlement (Refs. 10, 12 and 14). None of these programs have investigated the potential influence of strain rate on the degree of embrittlement. Fortunately, the tests conducted in these investigations were performed at relatively low strain rates. Unfortunately, since each

of the three investigators used different strain rates for tensile testing, direct comparison of their experimental results may not be possible. Test crosshead speeds used by these investigators ranged from 4×10^{-5} m/sec $(1 \times 10^{-1}$ in./min)(Ref. 10) to 3×10^{-7} m/sec $(7 \times 10^{-4}$ in./min)(Ref. 14).

Another investigation dealing with the influence of testing speed was discussed previously with respect to Figure 3(a). Fracture toughness tests were performed over a range of crosshead speeds. Embrittlement was more severe at lower crosshead speeds for each of the gas pressures used in the tests. The significance of these results is that test speed is an important experimental variable for tests utilizing precracked specimens as well as smooth bar tensile specimens.

Stress concentration factor. - A limited amount of research has been conducted on the influence of notch stress concentration factor on the severity of hydrogen environment embrittlement. The data shown in Figure 5 comparing tensile properties in hydrogen and in helium demonstrate that embrittlement in hydrogen is more severe for a notched specimen of A302-B steel than for a smooth specimen (Refs. 11 and 14). The tensile strength of a smooth specimen (a stress concentration factor of 1) is relatively unaffected by hydrogen. Embrittlement increases as the stress concentration factor increases from 1 to the range 4 to 6, but there does not appear to be any increased sensitivity at higher concentration factors of 8 or even for precracked specimens. Similar results were reported for A-517 steel (Refs. 11 and 14), for 4140 steel (Ref. 19), and for 304 L stainless steel (Ref. 19).

An even more sensitive measure of the severity of hydrogen environment embrittlement is the reduction of area of notched specimens. From the data presented in Figures 2 and 5, it is apparent that significant decreases in notched reduction of area occur during testing in hydrogen. Once again, it does not appear necessary to test specimens with extremely sharp notches. Notch stress concentration factors in the range 4 to 8 appear to be sufficient for determining the severity of hydrogen environment embrittlement.

Test temperature. - Only a limited amount of research has been conducted on the effect of test temperature on hydrogen environment embrittlement. The early data were determined over a relatively narrow range of test temperatures, -90° to 170° C, with CK 22 steel at a hydrogen pressure of 15 MN/m^2 (2200 psi)(Ref. 16). More recent research was performed over the temperature range -196° to 60° C with Inconel 718 and Ti-6Al-4V at a hydrogen pressure of 14 MN/m^2 (2000 psi) (Ref. 14). In all cases reductions in unnotched tensile ductility or notched tensile strength were more severe in the vicinity of room temperature.

Increased interest in recent years in using hydrogen for advanced rocket and gas-turbine engines has resulted in extensive investigations of the effect of hydrogen on structural materials over a much wider range of exposure temperatures. Materials of interest include steels (Refs. 3, 10 and 12), titanium alloys (Refs. 10 and 12), refractory metals (Ref. 6), and particularly, nickel- (Refs. 3, 10 and 12) and cobalt- (Refs. 3 and 13) base alloys.

The tensile properties of Inconel 718 tested over the temperature range

-196° to 525° C in hydrogen at 50 MN/m^2 (7500 psi) are presented in Figure 6 (Ref. 12). It is apparent from these data that reductions in both notched tensile strength and unnotched ductility are most severe near room temperature. However, significant embrittlement is still evident at substantially higher temperatures. In particular, the reduction of area of Inconel 718 at 525° C in hydrogen is about 67 percent of the value determined in air (Fig. 6(b)).

The tensile properties of Udimet 700 determined from 23° to 680° C in hydrogen at 30 to 50 MN/m^2 (4500 to 7500 psi) are presented in Figure 7 (Ref. 12). The extent of the embrittling effect of hydrogen on this alloy is far greater than for any other material reported to date. The notched tensile strength of Udimet 700 in hydrogen went through a minimum at about 200° C, and gradually approached the notched tensile strength determined in air as the test temperature was increased to 680° C (Fig. 7(a)). Moreover, the tensile properties of smooth specimens (ultimate strength, reduction of area, and elongation) were substantially reduced by hydrogen and remained at these low values over the entire range of test temperatures. For example, the elongation of Udimet 700 in hydrogen was about 3 percent for all test temperatures, as compared to about 20 percent in air (Fig. 7(b)). As mentioned previously during the discussion on hydrogen purity, these investigators did not find any difference in degree of embrittlement for Udimet 700 tested in dry hydrogen and water saturated hydrogen. Over the temperature range 150° to 305° C, there was also no effect of test temperature.

The results discussed above determined in dry hydrogen could not be

reproduced in another investigation (Ref. 13). Neither the smooth nor the notched tensile properties of Astroloy (Udimet 700) were reduced by more than 10 percent by testing in dry hydrogen at both 3.5 and 35 MN/m^2 (500 and 5000 psi) and at 23° and 680° C. Such lack of reproducibility may be due to either variations in alloy microstructure or hydrogen purity.

The effect of test temperature on the threshold stress intensity for crack initiation in Inconel 718 in hydrogen is shown in Figure 8 (Ref. 12). Sustained load, plane strain toughness test specimens were used to determine these data. The effect of temperature on the threshold stress intensity of this alloy is almost identical to the effect determined for tensile properties (see Fig. 6). Embrittlement is most pronounced near room temperature (K_{TH} = 33 $MN/m^{3/2}$ (30 ksi $\sqrt{in.}$)) and decreases at both lower and higher temperatures. A similar value of threshold stress intensity (K_{TH} = 24 $MN/m^{3/2}$ (22 ksi $\sqrt{in.}$)) at room temperature has been reported by others for Inconel 718 annealed at 954° C (Refs. 7 and 9).

Relative Sensitivity of Various Test Methods

From the data presented in the preceeding figures, it is evident that tensile tests have frequently been used to determine the extent of hydrogen environment embrittlement of metals. Large decreases in unnotched reduction of area, notched reduction of area, and notched tensile strength have been reported for various metals. Fracture toughness testing has also been shown to be a sensitive technique for determining the extent of hydrogen environment embrittlement. However, most investigators have utilized only one or two types of tests and, frequently, experimental vari-

ables differ among investigators so that comparison of data is difficult.

A recent investigation (Ref. 10) has used fatigue and creep testing in addition to tensile and fracture toughness testing to determine the relative susceptibility of various alloys to hydrogen environment embrittlement. It is informative to evaluate the relative sensitivity of all of these test methods. The degradation of various mechanical properties of Inconel 718 in hydrogen at a pressure of 35 MN/m^2 (5000 psi) is presented in Figure 9. It is immediately evident that substantial decreases in both low cycle (LCF) and high cycle (HCF) fatigue lives occur during testing in hydrogen. Both LCF (2000 cycles in helium) and HCF (50 000 cycles in helium) lives were reduced about 80 percent when tested at 26° C in hydrogen. At 680° C the LCF life (400 cycles in helium) was reduced about 30 percent and the HCF life (20 000 cycles in helium) was reduced about 96 percent.

These same investigators also showed that notched tensile properties and unnotched reduction of area at 26° C are substantially degraded by hydrogen, as has been discussed in several previous sections of this paper. The stress for 100 hour rupture life at 680° C also appeared to be reduced. All other properties were reduced by 10 percent or less. The negligible degradation of fracture toughness reported by these investigators is in marked contrast to the substantial decreases in the fracture toughness of Inconel 718 determined at room temperature by others (see previous section, Fig. 8 and Refs. 7, 9 and 12). Such lack of reproducibility may be due to material variations, or to slight differences in hydrogen pressure and purity.

A newly developed technique, the disk pressure test (Ref. 18), has

the appealing advantages of low cost, simplicity, and rapidity of testing. Small discs of sheet material are attached to a high pressure chamber by restrain at their periphery, and ruptured by introducing gaseous hydrogen into the chamber. Hydrogen pressure can be increased at a given rate until failure occurs, or held constant at very low pressures to determine the delayed failure characteristics of the material. For example, the delayed failure behavior of high-strength (2 GN/m^2 (300 ksi)) martensitic steel (4.3 Ni, 1.9 Cr, 0.5 Mo, 0.4 C, 0.37 Mn, 0.3 Si) is shown in Figure 10 (Ref. 18). These results determined during hydrogen environment testing are identical to results commonly encountered during testing for internal reversible hydrogen embrittlement. Figure 10 exhibits all the characteristics of the classical delayed failure tests determined with cathodically hydrogenated steels - a crack incubation period which is reversible with respect to applied stress (pressure), a region of slow crack growth followed by catastrophic failure, and a threshold stress (lower critical stress) below which crack growth and failure do not occur in a reasonable test time. Such similarities between hydrogen environment embrittlement and internal reversible hydrogen embrittlement have naturally been used by this investigator (Ref. 18) as evidence that these two types of embrittlement are analogous.

CONCLUDING REMARKS

In this paper the author has tried to lay the groundwork for subsequent discussions of mechanisms and the details of test specimens and test techniques for hydrogen environment embrittlement research. Both the effects of the experimental variables and test techniques used by previous investigators have been discussed. The results of both mechanistic and

screening studies have been described.

It is important to determine the effects of several experimental variables before attempting to standardize either test specimens or test techniques. The results determined to date regarding the degree of susceptibility of metals to hydrogen environment embrittlement are not reproducible among investigators. The author feels that both experimental and material variables may account for this observed lack of reproducibility. Therefore, it is suggested that the effects of experimental variables such as test strain rate, gas purity, specimen surface condition, hold time in the environment prior to testing, and baseline environment (air, helium, argon, or vacuum) be studied in more detail. The role of material microstructure, grain size, and grain boundaries is not well understood and requires additional research, possibly with directionally solidified alloys and single crystals. In addition to helping to resolve the lack of reproducibility of test results, greater knowledge of the precise influence of these variables would be invaluable in determining the mechanism of hydrogen environment embrittlement. Finally, in order to determine whether hydrogen environment embrittlement is distinct from internal reversible embrittlement, particular emphasis should be placed on the necessity for hydrogen diffusion through the lattice and the location of crack initiation during hydrogen environment embrittlement. It appears that the disk pressure and fracture toughness tests of various types have great potential for determining the influence of many of these experimental variables.

Both notched tensile and disc pressure testing appear to be suffi-

ciently sensitive to determine the occurrence of and the relative susceptibility of materials to hydrogen environment embrittlement at pressure below about 7 MN/m^2 (1000 psi). At higher pressures, standard unnotched tensile tests probably could also be used for screening purposes. All of these tests, however, should be conducted at low strain rates. Obviously, all mechanical testing should be conducted under simulated service conditions of gas pressure, gas purity, and temperature.

For more detailed investigations and prior to final design for service applications in hydrogen, it is suggested that fracture toughness, creep rupture, and/or fatigue tests be conducted. The choice of these tests should be dictated by the type of loading conditions that will be experienced in service. Once again it is extremely important for valid testing results that the hydrogen composition represent that to be encountered in service. If precracked specimens are to be tested, then they should be precracked and tested in the simulated service environment without any intermediate exposure to other environments.

<div align="center">REFERENCES</div>

1. McPherson, W. B. and Cataldo, C. E., ''Recent Experience in High Pressure Gaseous Hydrogen Equipment at Room Temperature,'' Technical Report No. D 8-14. 1, American Society for Metals, Metals Park, Ohio, Oct. 1968.

2. Laws, J. S., Frick, V. and McConnell, J., ''Hydrogen Gas Pressure Vessel Problems in the M-1 Facilities,'' NASA Report CR-1305, National Aeronautics and Space Administration, Washington, D. C., Mar. 1969.

3. Klima, S. J., Nachtigall, A. J. and Hoffman, C. A., "Preliminary Investigation of Effect of Hydrogen on Stress-Rupture and Fatigue Properties of an Iron-, a Nickel-, and a Cobalt-Base Alloy," NASA Report TN D-1458, National Aeronautics and Space Administration, Cleveland, Ohio, Dec. 1962.

4. Williams, D. P. and Nelson, H. G., Metallurgical Transactions, Vol. 1, No. 1, Jan. 1970, pp. 63-68.

5. Nelson, H. G., Williams, D. P. and Tetelman, A. S., Metallurgical Transactions, Vol. 2, No. 4, Apr. 1971, pp. 953-959.

6. Chandler, W. T. and Walter, R. J., "Hydrogen Effects in Refractory Metals," presented at the Symposium on Metallurgy and Technology of Refractory Metal Alloys, American Institute of Mining, Metallurgy and Petroleum Engineers and National Aeronautics and Space Administration, Washington, D.C., Apr. 25-28, 1968.

7. Lorenz, P. M., "Effect of Pressurized Hydrogen upon Inconel 718 and 2219 Aluminum," Technical Report D2-114417-1, NASA CR-100208, Boeing Company, Seattle, Wash., Feb. 1969.

8. Campbell, J. E., "Effects of Hydrogen Gas on Metals at Ambient Temperature," Technical Report DMIC S-31, Battelle Memorial Institute, Columbus, Ohio, 1970.

9. Walter, R. J., Hayes, H. G. and Chandler, W. T., "Influence of Gaseous Hydrogen on Metals," Technical Report R-8716, NASA, CR-119917, Rocketdyne, Canoga Park, Calif., May 1971.

10. Harris, J. A., Jr. and VanWanderham, M. C., "Properties of Materials in High Pressure Hydrogen at Cryogenic, Room, and Elevated Temperatures," Technical Report PWA-FR-4566, NASA CR-119884, Pratt & Whitney Aircraft, West Palm Beach, Fla., June 1971.

11. Walter, R. J. and Chandler, W. T., Materials Science and Engineering, Vol. 8, 1971, pp. 90-97.

12. Frick, V., Janser, G. R. and Brown, J. A., in Space Shuttle Materials, Vol. 3, Society of Aerospace Materials and Process Engineers, Azusa, Calif., 1971, pp. 597-634.

13. Harris, J. A., Jr. and VanWanderham, M. C., "Influence of Elevated Temperature on Metals in Gaseous Hydrogen," Technical Report PWA-FR-5082, Pratt & Whitney Aircraft, West Palm Beach, Fla., Apr. 1972.

14. Jewett, R. P., Walter, R. J., Chandler, W. T. and Frohmberg, R. P., "Hydrogen-Environment Embrittlement of Metals," NASA Technology Survey, Contract NAS8-19(C), Rocketdyne, Canoga Park, Calif., 1972.

15. Cavett, R. H. and Van Ness, H. C., Welding Journal, Welding Research Supplement, Vol. 42, July 1963, pp. 316s-319s.

16. Hofman, W. and Rauls, W., Welding Journal, Welding Research Supplement, Vol. 44, May 1965, pp. 225s-230s.

17. Hancock, G. G. and Johnson, H. H., Transactions, American Institute of Mining, Metallurgical and Petroleum Engineers, Vol. 236, No. 4, Apr. 1966, pp. 513-516.

18. Fidelle, J. P., Allemand, L. R., Roux, C. and Rapin, M., in
    Hydrogen in Metals, J. P. Fidelle and M. Rapin, eds., Valduc
    Colloquim, Commissariat a l'Energie Atomique, France, Sept.
    1967, pp. 131-172.

19. Vennett, R. M. and Ansell, G. S., Transactions Quarterly,
    American Society for Metals, Vol. 60, No. 2, June 1967,
    pp. 242-251.

20. Benson, R. B., Jr., Dann, R. K. and Roberts, L. W., Jr.,
    Transactions, American Institute of Mining, Metallurgical and
    Petroleum Engineers, Vol. 242, No. 10, Oct. 1968, pp. 2199-2205.

21. Spitzig, W. A., Talda, P. M. and Wei, R. P., Engineering Fracture
    Mechanics, Vol. 1, 1968, pp. 155-165.

22. Vennett, R. M. and Ansell, G. S., Transactions Quarterly, American
    Society for Metals, Vol. 62, No. 4, Dec. 1969, pp. 1007-1013.

23. Walter, R. J., Jewett, R. P. and Chandler, W. T., Materials
    Science and Engineering, Vol. 5, No. 2, Jan. 1970, pp. 98-110.

24. Fricke, E., Stuwe, H.-P. and Vibrans, G., Metallurgical Trans-
    actions, Vol. 2, No. 9, Sept. 1971, pp. 2697-2700.

25. Marcus, H. L. and Stocker, P. J., in Specialists Meeting on Stress
    Corrosion Testing Methods, Conference Proceedings No. 98,
    Advisory Group for Aerospace Research and Development, Paris,
    France, Jan. 1972, pp. 16-1 - 16-6.

26. Groeneveld, T. P., Fletcher, E. E. and Elsea, A. R., "A Study of
    Hydrogen Embrittlement of Various Alloys," Technical Report NASA
    CR-77374, Battelle Memorial Institute, Columbus, Ohio, June 1966.

TABLE I. - CHARACTERISTICS OF THE TYPES OF HYDROGEN EMBRITTLEMENT

Characteristics	Types of embrittlement		
	Hydrogen environment embrittlement	Internal reversible hydrogen embrittlement	Hydrogen reaction embrittlement
Usual source of hydrogen	Gaseous (H_2)	Processing ⎫ Electrolysis ⎬ (H) Corrosion ⎭	Gaseous or atomic hydrogen from any source
Typical conditions	10^{-6} to 10^8 N/m^2 gas pressure Most severe near room temperature Observed -100° to 700° C Gas purity is important Strain rate is important	0.1 to 10 ppm average H content Most severe near room temperature Observed -100° to 100° C Strain rate is important	Heat treatment or service in hydrogen, usually at elevated temperatures
Test methods	Notched tensile Unnotched tensile Creep rupture Fatigue (low, high cycle) Fracture toughness Disk pressure test	Notched delayed failure Slow strain rate tensile Bend tests C-rings Torqued bolts	Can be observed visually or metallographically
Crack initiation	(Surface or internal initiation)[a]	Internal crack initiation -Incubation (reversible) -Slow, discontinuous growth -Fast fracture	Usually internal initiation from bubbles or flakes
Rate controlling step	Adsorption = transfer step $\left(\begin{array}{c}\text{Absorption or}\\\text{lattice diffusion}\end{array}\right)^a =$ embrittling step	Lattice diffusion to internal stress raisers	Chemical reaction to form hydrides or gas bubbles

[a]Unresolved

TABLE II. - METALS AND ALLOYS EMBRITTLED BY HYDROGEN

| Hydrogen environment embrittlement[a, b]	Internal reversible hydrogen embrittlement[a, c]	Hydrogen reaction embrittlement

High strength steels
  18Ni Maraging
  410, 440C, 430F
  H-11, 4140, 1042 (Q&T)
  Fe-9Ni-4Co, 17-7PH
	High strength steels
	  4340, 4140, H-11
	  17-4PH, AM 355
	  18Ni Maraging
	  E8740, 17-7PH
		1. Hydride embrittlement (MH$_x$)
		
		  (a) H reacts with matrix
		    Ti, Zr, Hf, V, Nb, Ta
		    Mn, Ni, Pd, U, Pu, Th
		    Rare earths

Nickel and nickel alloys
  Electroformed Ni
  Nickel 200, 270
  Inconel 625, 700, 706, 718
  Rene 41, Hastelloy X
  Udimet 700, Waspaloy
  MAR M-200DS, IN 100
	Exp. Fe-Ni-Cr alloys
	
	Exp. Fe-Cu alloys
		Alkalines
		    Alkaline earths
		
		  (b) H reacts with element in matrix
		    MgZr, MgTh alloys
		
		2. High pressure gas bubbles

Low strength steels
  Armco iron, CK22, CK45, 1020
  1042 Nor., HY-80, HY-100
  A-302, A-515, A-517
	Ti, Zr, V, Nb, Ta
	Cr, Mo, W, Co, Ni
	Pt, Cu, Au, Al, Mg
		(a) H reacts with itself (H_2)
		    Steels, OFHC Cu
		    Ni, Al, Mg, Be

Titanium alloys
  Ti-6Al-4V, Ti-5Al-2.5Sn
	and/or some of
	their alloys
		(b) H reacts with foreign element
		    in matrix

Cobalt alloys
  HS-188, L-605, S-816
	Metastable stainless steels
	  304L, 310
		CH$_4$ -- low alloy steels, Ni alloys

Metastable stainless steels 304L, 305, 310	K-Monel	H$_2$O -- welded steels, Cu, Ni, Ag
K-Monel Be-Cu Alloy 25 Pure titanium	High strength nickel alloys Inconel 718	

Stable stainless steels
  316, 321, 347, A-286
  Armco 21-6-9
	Rene 41
	  Waspaloy	

Copper alloys, OFHC Cu		

Aluminum alloys
  1100, 2219, 6061, 7039, 7075
	Stable austenitic steels
	  316, A-286, U-212	

[a]Listed in approximate order of decreasing susceptibility at room temperature.
[b]Most alloys from Refs. 14 and 23.
[c]Most steels and nickel-base alloys from Ref. 26.

TABLE III. - DEGRADATION OF NOTCHED TENSILE

PROPERTIES OF INCONEL 718

(Hydrogen pressure 35 MN/m^2 (5000 psi), 23° C, stress concentration factor (K_t) = 8 (Ref. 9)).

Material form	Ratio of property in hydrogen/in helium			
	Notch tensile strength		Notch reduction of area	
	940° C anneal	1050° C anneal	940° C anneal	1050° C anneal
Bar	0.54	0.71	0.31	0.34
Forging	.59	.76	.37	.39
Plate	.86	.77	.67	.62
Plate-weld metal	.79	.56	.71	.31
Plate-heat affected zone	.63	.72	.39	.29

	HYDROGEN MOLECULE
	HYDROGEN ATOM
○	OXIDE
o	LATTICE ATOM
⊛	SUBSTITUTIONAL ⎤ ALLOYING OR
×	INTERSTITIAL ⎦ IMPURITY ATOM
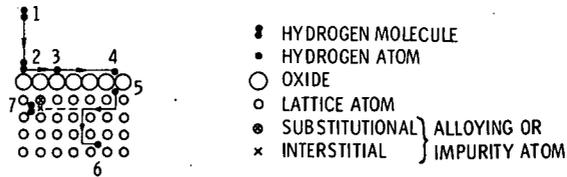
		OCCURRENCE OF EMBRITTLEMENT STEPS		
		TYPES OF EMBRITTLEMENT		
STEPS NECESSARY FOR EMBRITTLEMENT		HYDROGEN ENVIRONMENT	INTERNAL REVERSIBLE	HYDROGEN REACTION
1→2 MOLECULAR PHYSISORPTION	⎫	YES	NO	YES/NO
2→3 DISSOCIATION	⎬ ADSORPTION	YES	NO	YES/NO
3→4 CHEMISORPTION	⎭	YES	NO	YES/NO
4→5 SOLUTION (ABSORPTION)		YES	YES	YES
5→6 LATTICE DIFFUSION		?	YES	YES
5/6→7 HYDROGEN REACTION TO FORM HYDRIDES AND/OR GAS BUBBLES		NO	NO	YES

Figure 1. - Physical and chemical processes necessary for various types of hydrogen embrittlement (after ref. 5).
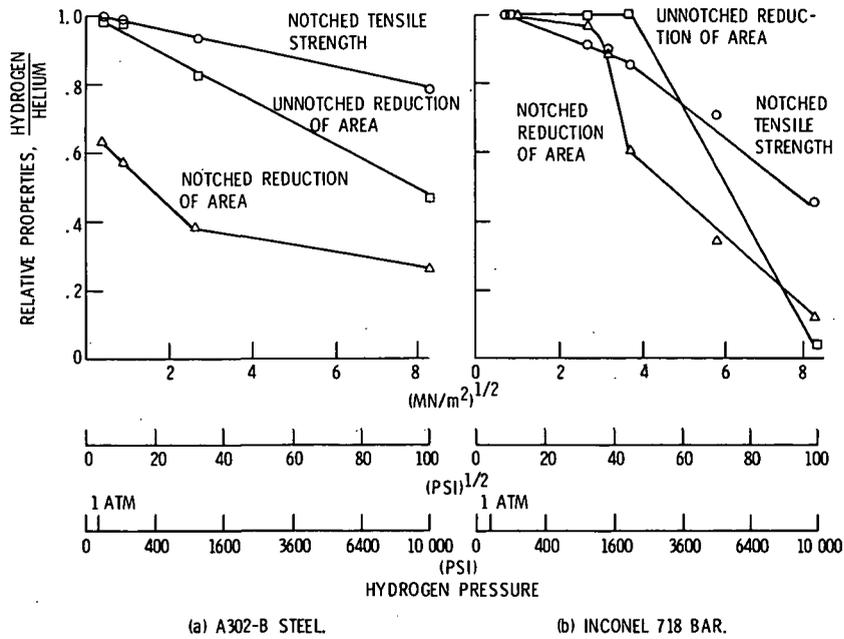
Figure 2. - Effect of gas pressure on tensile properties of A302-B steel (ref. 14) and Inconel 718 (refs. 9 and 14) at 23° C. Inconel bar annealed at 1050° C; notched specimens, $K_t = 8$.

(a) A302-B STEEL.

(b) INCONEL 718 BAR.

(a) EFFECT OF TEST SPEED AT 23° C.

(b) EFFECT OF TEMPERATURE AT A CROSSHEAD SPEED OF 1.3x10⁻⁶ m/SEC.
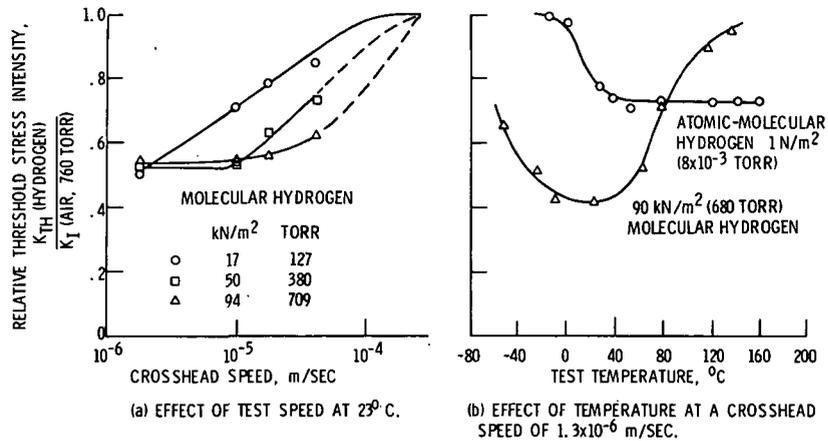
Figure 3. - Effect of crosshead speed, test temperature, hydrogen pressure, and hydrogen composition on threshold stress intensity (K_{TH}) of 4130 steel. (Refs. 4 and 5.)
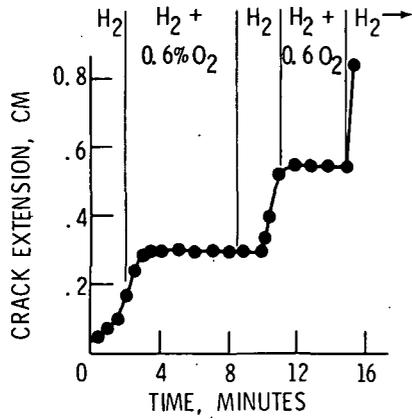
Figure 4. - Effect of hydrogen purity on crack growth in H-11 steel at 23° C and a hydrogen pressure of 0.1 MN/m^2 (15 psi)(ref. 17).
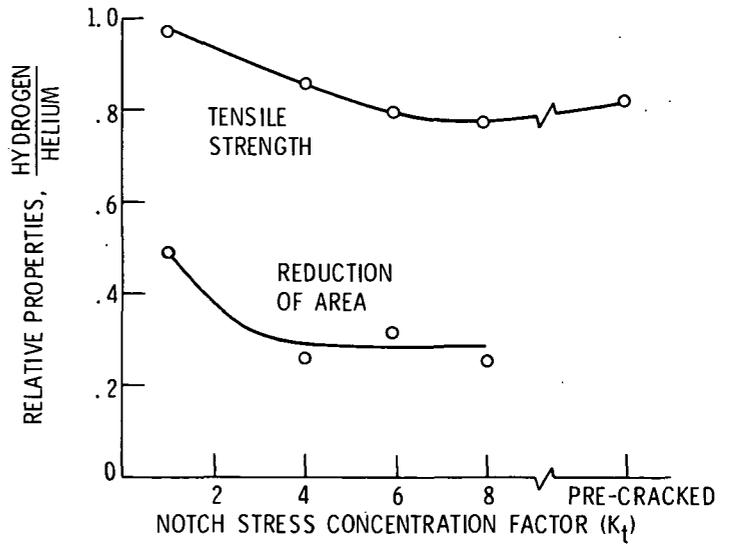
Figure 5. - Effect of notch stress concentration factor (K_t) on tensile properties of A302-B steel at 23° C determined in hydrogen and helium at a pressure of 70 MN/m^2 (10 000 psi)(refs. 11 and 14).


(a) STRENGTH.

(b) UNNOTCHED DUCTILITY.
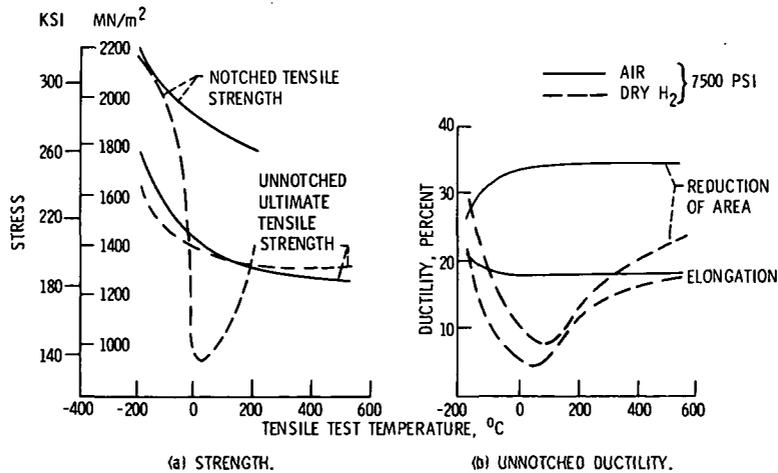
Figure 6. - Effect of test temperature on tensile properties of Inconel 718 bar at a hydrogen pressure of 50 MN/m^2 (7500 psi)(ref. 12). Alloy annealed at 954° C; notched specimens, K_t = 8.
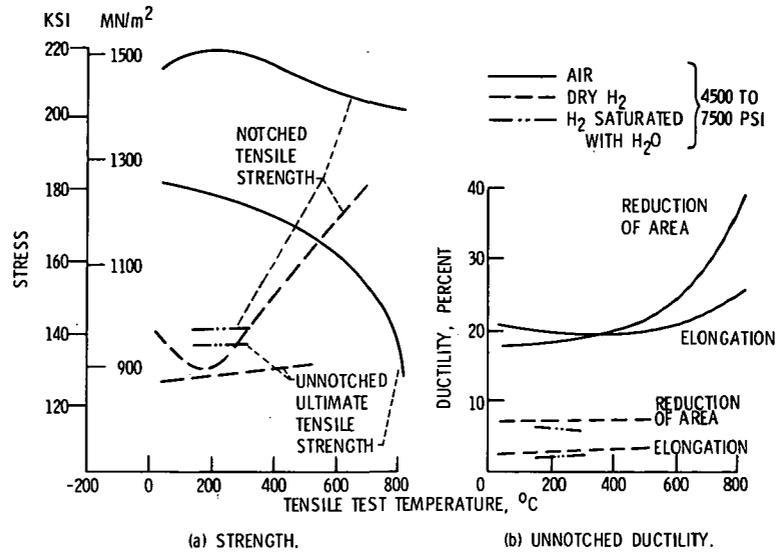
Figure 7. – Effect of test temperature on tensile properties of Udimet 700 at a hydrogen pressure of 30 to 50 MN/m^2 (4500 to 7500 psi)(ref. 12). Notched specimens, K_t = 8.
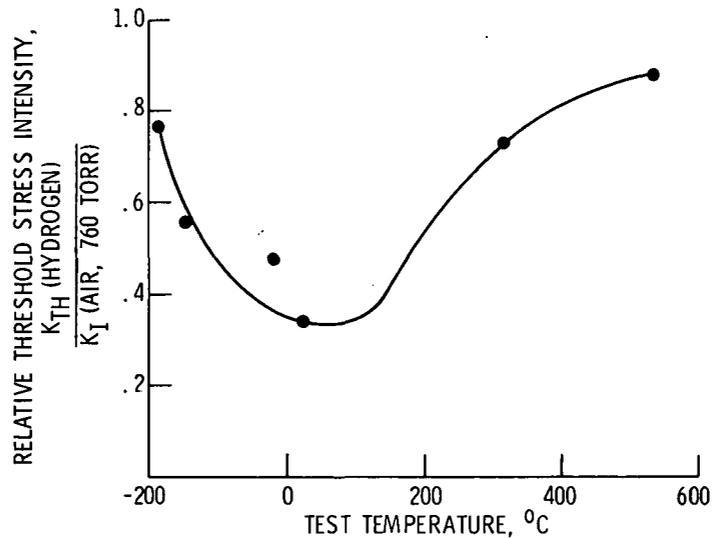

Figure 8. – Effect of test temperature on threshold stress intensity (K_{TH}) of Inconel 718 plate at a hydrogen pressure of 50 MN/m^2 (7500 psi)(ref. 12). Alloy annealed at 1066° C.
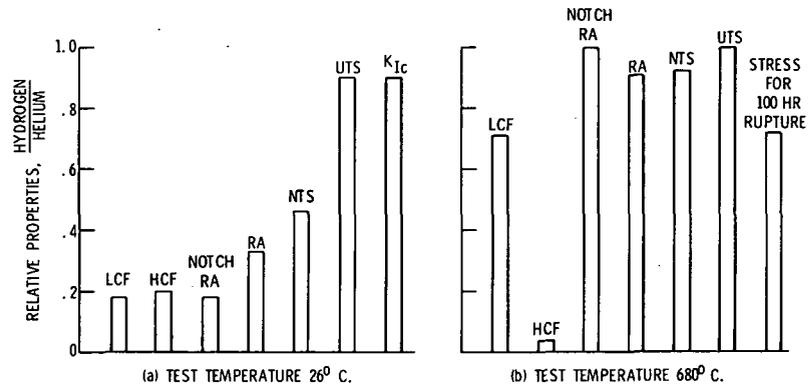
Figure 9. - Comparison of mechanical properties of Inconel 718 bar determined in hydrogen and helium at a pressure of 35 MN/m² (5000 psi)(ref. 10). Alloy annealed at 1038° C; notched specimens, K_t = 8; LCF, 1-2% strain, HCF, R = 0.1, (a) 180 ksi, (b) 140 ksi.
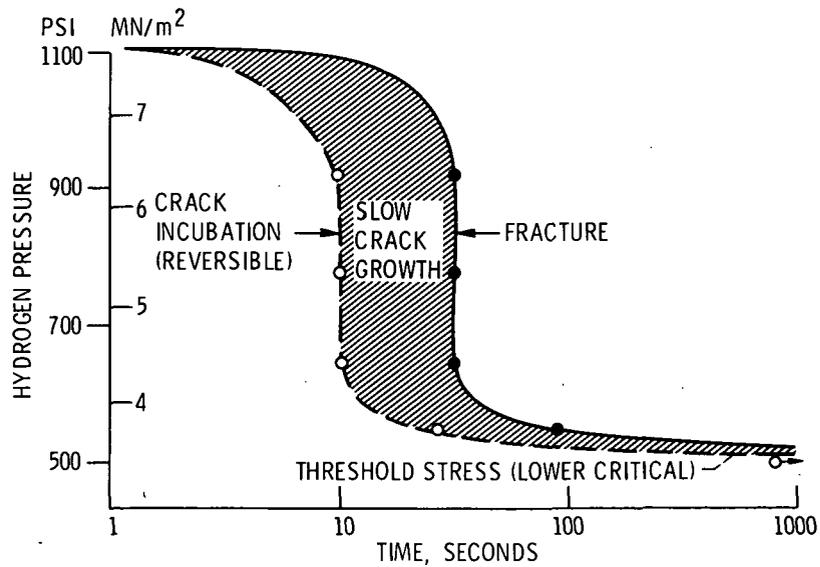

Figure 10. – Effect of hydrogen pressure on the delayed failure of 35 NCD 16 steel at 23° C determined by the disc pressure test (ref. 18).