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HYDROGEN EMBRITTLEMENT OF STRUCTURAL ALLOYS – A TECHNOLOGY SURVEY

By James L. Carpenter, Jr., and William F. Stuhrke

MARTIN MARIETTA CORPORATION
Orlando Division
Orlando, Florida 32805

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16 Abstract

This Technology Survey Report is comprised of reviewed and evaluated technical abstracts for about 90 significant documents relating to hydrogen embrittlement of structural metals and alloys. Particular note was taken of documents regarding hydrogen effects in rocket propulsion, aircraft propulsion and hydrogen energy systems, including storage and transfer systems.

The abstracts in the report are selected from the pertinent literature published between April 1962 and December 1975 with most attention devoted to the last five years. The purpose of this report is to provide, in quick reference form, a dependable source for current information in the subject field.

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FOREWORD

This Technology Survey was prepared by Martin Marietta Aerospace under Contract NAS 3-19530. It is one product of a research program initiated by the NASA Lewis Research Center to compile, evaluate, and organize for convenient access information on the mechanics of structural failure and structural materials limitations. The NASA Aerospace Safety Research and Data Institute (ASRDI) has technical responsibility for the research program. Preparation of this report was under the direction of George Mandel, ASRDI Program Manager.

Many people contributed to the preparation of the report. Their assistance and cooperation is appreciated and gratefully acknowledged. The authors wish to especially acknowledge the interest and assistance of the following individuals: H. Dana Moran, Battelle Memorial Institute; James H. Swisher, Energy Research and Development Administration; John A. S. Green, H. Wayne Hayden, and Judy Watts, Martin Marietta Laboratories; Anthony W. Thompson, Rockwell Science Center; John B. Greer, ESSO Production Research Center; and Hugh R. Gray, NASA Lewis Research Center.

KEY WORDS

Analysis methods; brittle fractures; chemical reactions; dislocations (materials); embrittlement; environment effects; gas embrittlement; high strength alloys; hydrogen; hydrogen charging; hydrogen embrittlement; hydrogen environment embrittlement; material defects; mechanisms, metallic materials, stress corrosion cracking; stress intensity factor; testing methods.

PREFACE

Since June 1972 the Orlando Division of Martin Marietta Aerospace has supported the NASA Lewis Research Center's Aerospace Safety Research and Data Institute (ASRDI) in an investigation of the mechanics of structural failure and structural materials limitations. A series of technical reports have been produced.

Under Contract NAS 3-16681 an initial Register of Experts for Information on the Mechanics of Structural Failure was published as NASA CR-121200. An updated and enlarged version was published in January 1975 as NASA CR-134754. Its purpose was to give visibility for a listing of recognized experts who might be available for consultation related to the mechanics of structural failure. Contract NAS 3-16680 also produced other products: NASA CR-121201, Register of Sources for Information on the Mechanics of Structural Failure; NASA CR-121202, Bibliography of Information on the Mechanics of Structural Failure; and NASA CR-12199, Thesaurus of Terms of Information on the Mechanics of Structural Failure. The last of these reports is comprised of key words which facilitate access to an ASRDI mechanized data base.

This Technology Survey Report is one of a series of such reports prepared under Contracts NAS 3-17640 and NAS 3-19530. Other technology reports and companion bibliographies include: NASA CR-134760, Life Prediction of Materials Exposed to Monotonic and Cyclic Loading - A Technology Survey; NASA CR-134751, Life Prediction of Materials Exposed to Monotonic and Cyclic Loading - A Bibliography; NASA CR-134752, Fracture Toughness Testing Data - A Technology Survey; NASA CR-134753, Fracture Toughness Testing Data - A Bibliography; NASA CR-134962, NDE-An Effective Approach to Improved Reliability and Safety - A Technology Survey; and NASA CR-134964, Bibliography of Information on Mechanics of Structural Failure (Hydrogen Embrittlement, Protective Coatings, Composite Materials, NDE).

The report is comprised of interpreted abstracts of about 90 key documents related to hydrogen effects of structural materials. These documents have been surfaced and selected in a literature search performed between June 1972 and December 1975. Since a significant number of the documents relate to more than one aspect of hydrogen embrittlement there are often multiple citations of the same document. All of the documents selected and abstracted for this technology survey report are included in ASRDI's mechanized data base. In addition a majority of the references cited with the abstracted documents are also included in the ASRDI data bank. This affords a significant information resource for the interested researcher.

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INTRODUCTION-OVERVIEW OF THE REPORT

INTRODUCTION - OVERVIEW OF THE REPORT

The effect of hydrogen embrittlement on structural metals has recently become a subject of significant interest due to the potential of hydrogen as a primary energy source. An understanding of hydrogen effects is particularly important to the designers and operators of hydrogen propulsion systems and hydrogen storage and transfer systems.

The characterization and assessment of the role of hydrogen in the behavior of materials is the subject of much controversy. There are proponents of pressure theories, decohesion theories, and compound theories. Acceptance of these theories and hypotheses is complicated by knowledge of the various forms of diffusion transport and particularly by the relatively new understanding of dislocation transport of hydrogen, including annihilation. Another complication is the need for and use of complex mathematical models to describe hydrogen embrittlement mechanisms or to analyze proposed theories. These range from the fracture mechanics/diffusion/decohesion analysis methodology in use at Brown University to the statistical modeling of J. K. Tien of Columbia University and H. P. Van Leeuwen of the National Aerospace Laboratories, Amsterdam (Netherlands).

The authors of this report have summarized the current body of knowledge on hydrogen embrittlement in structural alloys as it is expressed in the literature of the past decade. The report is only a contribution toward the establishment of a larger and much needed information base. Nevertheless it is felt that the contribution is substantive and that it will cause the publication of other related, valuable knowledge. To introduce the abstracts which form the main text of the report, the authors have written an overview of the key contributions of the researchers represented by the abstracts. Also, a reference list is included to substantiate the authors' conclusions.

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Hydrogen is the first element in the periodic table and is the simplest atomic structure. Except at temperatures within a few degrees of absolute zero it is a gas which forms compounds readily with most elements. In addition, because of its small atomic size, it penetrates metallic lattices at a rapid rate significantly influencing the mechanical properties of the host material.

The influence of hydrogen on the behavior of metals has long been accepted as the sources of various types of problems including material failures. Dr. A. R. Troiano, in 1974, pointed out that these phenomena were recognized over 100 years ago (ref. 1). At that time it was

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demonstrated that iron was subject to what we characterize today as reversible damage, brittle delayed failure, environmental degradation (stress corrosion cracking), and irreversible embrittlement. The metals processing, chemical, and petrochemical industries have lived with these phenomena in an empirical manner for many years. Their experience has resulted in compilation of a large amount of information on the use of structural materials in certain services and a well-founded basis for restricting the uses of some materials.

In the late nineteen-fifties, because of pressures from the rapidly expanding aerospace industry, brittle failure due to hydrogen effects became the subject of more intense study. This activity was summarized in Troiano's Campbell Memorial Lecture in 1960 (ref. 2). In that milestone presentation the primary role of hydrogen in various types of embrittlement situations was illustrated.

The increasing costs of energy both in terms of nonrenewable resources and pollution control has introduced a new dimension to the investigation of hydrogen effects on materials. The field has been brought more sharply into focus in the past two years in three symposia (ref. 3, 4, 5). These meetings revealed most of the new knowledge that has come of the several years of intensive research since the mid-sixties which enable us to now characterize the effects of hydrogen on metallic materials as they are described in this report.

To facilitate communication, the authors have elected to use the three definitions of embrittlement proposed by H. R. Gray (ref. 6):

- Internal reversible hydrogen embrittlement (IHE)
- Hydrogen environment embrittlement (HEE)
- Hydrogen reaction embrittlement (HRE)

Definitions for the three types of embrittlement follow:

<u>Internal reversible hydrogen embrittlement (IHE)</u>. This has been termed slow strain rate embrittlement and/or delayed failure, and as the classical type, it has been studied extensively. Hydrogen may be charged into the metal due to electroplating, processing treatments such as melting and pickling, or stress-corrosion processes that result in the production of hydrogen as an active species. Reversible embrittlement requires that the hydrogen does not experience any chemical reaction while contained as a diffusable specie within the metal lattice.

<u>Hydrogen environment embrittlement (HEE)</u>. This type was first recognized as a serious problem after the failure of high pressure hydrogen storage tanks (ref. 7). There is some disagreement over the mechanism, however it is always associated with a gaseous hydrogen environment. In addition it is observed to occur in nickel alloys which are relatively insensitive to IHE.

Hydrogen reaction embrittlement (HRE). In this type of embrittlement, hydrogen may react near the surface or diffuse substantial distances into the lattice before it reacts. Hydrogen can react with itself, with the matrix, or with a foreign element in the matrix. The new phases formed by these reactions are stable and the embrittlement is normally not reversible during room temperature aging treatments.

In addition, major consideration is given to three specific hydrogen effects which have received widespread attention:

- Stress corrosion cracking (SCC)
- Crack growth and fracture mechanics
- Ductile fracture

These three effects are defined as follows:

Stress corrosion cracking (SCC). An important change in the understanding of the effects of hydrogen has been the change from considerable controversy to a general acceptance of the primary role of hydrogen in SCC. The role of hydrogen is particularly important when SCC refers to a brittle type delayed failure under stress and not to situations where failure occurs by corrosion which is accelerated by stress. Recent work by John A. S. Green and his coworkers (ref. 8) has led to a very definitive test which conclusively proves the controlling nature of the role of hydrogen in SCC.

Crack growth/fracture mechanics. The behavior of subcritical crack growth in the presence of hydrogen has been shown to be a function of the fracture mechanics stress intensity factor K (ref. 9). It has also been shown that the degree of embrittlement observed in any particular circumstances depends on three factors: the stress at which the hydrogen-induced crack initiates, the rate of slow crack growth, and the length to which the crack must grow to instigate catastrophic failure (ref. 10).

Ductile failure. The influence on what is called the ductile failure of metals in the presence of hydrogen has been only recently appreciated (ref. 11). This phenomena has been observed in nickel alloys, and also in austenitic stainless steels which had been thought to be immune to hydrogen embrittlement. In these cases fracture occurs by an accelerated ductile rupture process. The total reduction in area is typically reduced and in some cases the fracture surface shows some evidence of brittle failure on a microscale.

The effect of hydrogen on specific alloy systems is now reasonably well characterized (ref. 12). It has been shown that almost all commercially important structural alloy systems are affected by hydrogen in some way. These are summarized below:

Structural steels. These metal alloys are subject to HEE, IHE and HRE. The IHE is usually more severe at the higher strength levels. A very important hydrogen problem for this class of materials is the hydrogen sulfide problem encountered in the petrochemical industry (ref. 13). In this hydrogen sulfide environment the steels exhibit stress corrosion cracking which can lead to an accelerated local failure. It is empirically controlled by reducing stress levels and careful control of the metallurgical factors of the steel. One of the properties employed in this control is hardness.

Ultrahigh strength steels. These high strength materials demonstrate the classical IHE in which delayed brittle failure and significantly decreased fracture toughness are found (ref. 14). The significant embrittlement results from the internal absorption of hydrogen prior to the application of external stress. The average amount of hydrogen may be very small, being on the order of less than 0.1 ppm; however, this amount is concentrated several orders of magnitude at crack tips or other defects in the lattice structure. The resulting failure is due to either hydrogen pressure buildup at the tip of the advancing crack or a combination of pressure and lattice decohesion resulting from a lowering of the surface energy required for crack growth (ref. 15). In addition significant ductility and strength losses and increases in crack growth rate for these materials in the presence of a hydrogen atmosphere (HEE) have been observed (ref. 16).

Stainless steels. These steels, alloyed with various amounts of chromium and nickel, are available with three types of microstructure each with different degrees of susceptibility to hydrogen embrittlement. The high strength martensitic stainlesses exhibit a behavior similar to the ultra-high strength steels. The ferritic stainlesses are similar to the structural steels. The austenitic stainless steels are relatively immune to hydrogen embrittlement (ref. 11). However, it is becoming apparent that significant ductility losses and increases in crack growth rate resulting from HEE are occurring (ref. 11, 17, 18).

Titanium Alloys. The effect of hydrogen on titanium and its alloys was summarized by Paton and Williams in a 1974 symposium (ref. 19). Titanium is susceptible to HRE due to the formation of the α hydride phase. This titanium hydride is an ordered compound which is stable over the composition range of from $TiH_{1.53}$ to $TiH_{1.99}$. The hydride has a lower density than the titanium and is brittle. Under certain conditions it has been shown that once the crack is initiated it will propagate with no external stress over a wide range of environmental hydrogen pressures (ref. 20).

Nickel Alloys. The role of hydrogen in reducing the ductility of nickel alloys has been studied extensively. A comprehensive review by Smith (ref. 21), emphasizes the fact that there appears to be a need for some plastic deformation to initiate and continue hydrogen induced cracking.

Aluminum and its alloys. The susceptibility of aluminum alloys to hydrogen has now been established after considerable controversy. Aluminum alloys are susceptible to reversible embrittlement by diffusible hydrogen driven into the lattice when the fugasity of the hydrogen species in the surrounding environment is sufficiently high. Stress corrosion cracking has been attributed to hydrogen as liberated from aqueous solutions (ref. 22).

Gray has characterized the three types of hydrogen embrittlement (IHE, HEE, HRE) in detail in the American Society for Testing and Materials Special Technical Publication Number 543, (ref. 23). Table 1 in that report provides an excellent summary.

Several investigators have recently applied powerful theoretical mathematical analysis to the motion of hydrogen in metals (ref. 24, 25). In these analyses a theoretical basis for hydrogen motion and effects is being developed which will provide further help in the continuing effort to improve materials behavior. In addition some recent work promises to refine our ability to detect small quantities of hydrogen in the metal lattice (ref. 26). These techniques coupled with the developing technology of nondestructive evaluation offer promise for improved control, alloy design, and structural design of materials for hydrogen service.

References:

1. Troiano, A. R., General Keynote Lecture, Hydrogen in Metals, Proc. Int. Conf. on the Effects of Hydrogen on Materials Properties and Selection and Structural Design, Champion, PA (September 23-27, 1973).

2. Troiano, A. R., The Role of Hydrogen and Other Interstitials in the Mechanical Behavior of Metals, Edward DeMille Campbell Memorial Lecture, Trans. ASM 52, 54 (1960).

3. Hydrogen Embrittlement Testing, ASTM STP-543 (1974)

4. Hydrogen In Metals, Proc. Int. Conf. on the Effects of Hydrogen on Materials Properties and Selection and Structural Design, Champion, PA, (September 23-27, 1973).

5. Proc. Int. Conf. on Effect of Hydrogen on Behavior of Materials, Moran, WY (September 7-11, 1975).

6. Gray, H. R., Opening Remarks, Hydrogen Embrittlement Testing, ASTM STP-543 (1974).

7. Laws, J. S., Frick, V. and McConnell, J., Hydrogen Gas Pressure Vessel Problems in the M-1 Facilities, NASA CR-1305, National Aeronautics and Space Administration (March 1969).

TABLE 1–Characteristics of the Types of Hydrogen Embrittlement

	Types of Embrittlement		
Characteristics	Hydrogen Environment Embrittlement	Internal Reversible Hydrogen Embrittlement	Hydrogen Reaction Embrittlement
Usual source of hydrogen	gaseous (H_2)	processing, electrolysis, corrosion (H)	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^o to 700^oC gas purity is important strain rate is important	0.1 to 10 ppm average H content most severe near room temperature observed -100^o to 100^oC 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)*	internal crack initiation incubation (reversible) slow, discontinuous growth fast fracture	usually internal initiation from bubbles or flakes
Rate controlling step	adsorption = transfer step (absorption or lattice diffusion)* = embrittling step	lattice diffusion to internal stress raisers	chemical reaction to form hydrides or gas bubbles

*Unresolved.

8. Green, J. A. S., Hayden, H. W., and Montague, W. G., Stress-Corrosion Cracking Mechanisms in 7075-T6 Aluminum Alloy, Proc. of Int. Conf. on Effect of Hydrogen on Behavior of Materials, Moran, WY (September 7-11, 1975).

9. Gangloff, R. P., and Wei, R. P., Embrittlement of 18Ni Maraging Steel by Low Pressure Gaseous Hydrogen, Proc. Int. Conf. on Effect of Hydrogen on Behavior of Materials, Moran, WY (September 7-11, 1975).

10. Hardie, D. and Bowker, R., The Effect of a Gaseous Hydrogen Environment on the Fracture Behavior of HY-150 Type Steel, Proc. Int. Conf. on Effect of Hydrogen on Behavior of Materials, Moran, WY (September 7-11, 1975).

11. Thompson, A. W., Ductility Losses in Austenitic Stainless Steels Caused by Hydrogen, Hydrogen in Metals, Proc. Int. Conf. on the Effects of Hydrogen on Materials Properties and Selection and Structural Design, Champion, PA (September 23-27, 1973).

12. Bernstein, I. M. and Thompson, A. W., Alloy Design to Resist Hydrogen Embrittlement, Strengthening Mechanisms and Alloy Design, Edited by J. K. Tien and G. S. Ansell, Academic Press (1975).

13. Greer, J. B., Factors Affecting the Sulfide Stress Cracking Performance of High Strength Steels, Materials Performance, NACE (March 11-12, 1975).

14. Tetelman, A. S., Recent Developments in Classical (Internal) Hydrogen Embrittlement, Hydrogen in Metals, Proc. Int. Conf. on the Effects of Hydrogen on Materials Properties and Selection and Structural Design, Champion, PA (September 23-27, 1973).

15. Tetelman, A. S., The Mechanism of Hydrogen Embrittlement in Steel, in Fundamental Aspects of Stress Corrosion Cracking, 446-460, NACE, (1969).

16. Johnson, H. H., Hydrogen Gas Embrittlement, Hydrogen in Metals, Proc. Int. Conf. on the Effects of Hydrogen on Materials Properties and Selection and Structural Design, Champion, PA (September 23-27, 1973).

17. Louthan, Jr., M. R., Effects of Hydrogen on the Mechanical Properties of Low Carbon and Austenitic Steels, Hydrogen in Metals, Proc. Int. Conf. on the Effects of Hydrogen on Materials Properties and Selection and Structural Design, Champion, PA (September 23-27, 1973).

18. Thompson, A. W., The Mechanism of Hydrogen Participation in Ductile Fracture, Proc. Int. Conf. on Effect of Hydrogen on Behavior of Materials, Moran, WY (September 7-11, 1975).

19. Paton, N. E. and Williams, J. C., Effect of Hydrogen on Titanium and its Alloys, Hydrogen in Metals, Proc. Int. Conf. on the Effects of Hydrogen on Materials Properties and Selection and Structural Design, Champion, PA (September 23-27, 1973).

20. Cox, T. B. and Gudas, J. P., Investigation of the Fracture of Near-Alpha Titanium Alloys in High Pressure Hydrogen Environments, Proc. Int. Conf. Effect of Hydrogen on Behavior of Materials, Moran, WY (September 7-11, 1975).

21. Smith, G. C., Effect of Hydrogen on Nickel and Nickel-Base Alloys, Hydrogen in Metals, Proc. Int. Conf. on the Effects of Hydrogen on Materials Properties and Selection and Structural Design, Champion, PA (September 23-27, 1973).

22. Speidel, M. O., Hydrogen Embrittlement of Aluminum Alloys, Hydrogen in Metals, Proc. Int. Conf. on the Effects of Hydrogen on Materials Properties and Selection and Structural Design, Champion, PA (September 23-27, 1973).

23. Gray, H. R., Testing for Hydrogen Environment Embrittlement: Experimental Variables, Hydrogen Embrittlement Testing, ASTM STP-543, 133-151 (1974).

24. Tien, J. K., Diffusion and Other Mechanisms of Hydrogen Transport, Proc. Int. Conf. on Effect of Hydrogen on Behavior of Materials, Moran, WY (September 7-11, 1975).

25. Van Leeuwen, H. P., An Analysis of Hydrogen-Induced Cracking, Proc. Int. Conf. on Effect of Hydrogen on Behavior of Materials, Moran, WY (September 7-11, 1975).

26. Toy, S. M., Neodymium Detection System, Hydrogen Embrittlement Testing, ASTM STP-543, 124-130 (1974).

I. STATE OF THE ART REVIEWS AND OVERVIEWS

HYDROGEN GAS EMBRITTLEMENT

Johnson, H. H. (Cornell Univ., Ithaca, NY)

Proc. Int. Conf. Effects of Hydrogen on Material Properties and Selection and Structural Design, Champion, PA (23-27 September 1973)

It has been established in the past decade that external hydrogen gas causes brittleness in many alloy systems including titanium and titanium alloys, and nickel and nickel-base alloys. Hydrogen pressures from much less than 1 atm (10^5 N/m^2) to 10,000 psi (6.8 X 10^7 N/m^2) have been used, and it is clear that in general susceptibility to hydrogen gas increases with pressure. Parameters measured as indices of brittleness include elongation, reduction of area, notch tensile strength, time to failure, crack growth rate, threshold stress and threshold stress intensity. In common with classical hydrogen brittleness, the notch and flaw-associated properties are far more sensitive to hydrogen gas than are the unnotched properties, and brittleness is more evident in high strength alloys than low strength alloys. The analysis suggests that brittleness may result whenever material under very high stress is exposed to hydrogen. In high strength materials very high local stresses may be expected because of the complex microstructures associated with high strength levels. In lower strength materials plastic deformation may be expected to intervene before very high local stresses are developed. This suggests that whiskers of metals normally soft in bulk form might well be brittle in the presence of hydrogen gas, since very high stresses may be attained in whiskers. It also suggests that experimental studies of the interaction between hydrogen and unstressed material will not provide information directly relevant to hydrogen brittleness.

Comment:

The author reports on an extensive amount of research experience which established hydrogen gas as the factor in the embrittlement of many metallurgical alloy systems. The observation on the role of stress level in embrittlement is particularly important. Johnson's work suggests that hydrogen gas embrittlement may become more prevalent as metals are used at higher strength in more critical applications.

Important References:

1. Hancock, G. G. and Johnson, H. H., Hydrogen, Oxygen and Subcritical Crack Growth in High-Strength Steel, Trans. Met. Soc. AIME 236, 513-516 (1966).

2. Williams, D. P. and Nelson, H. G., Embrittlement of 4130 Steel by Low-Pressure Gaseous Hydrogen, Met. Trans. 1, 63-68 (1970).

3. Nelson, H. G., Williams, D. P., and Stein, J. E., Environmental Hydrogen Embrittlement of an Alpha-Beta Titanium Alloy Effect of Microstructure, Met. Trans. 3, 469-475 (1972).

4. Williams, D. P. and Nelson, H. G., Gaseous Hydrogen-Induced Cracking of Ti-5Al-2.5 Sn, Met. Trans. 3, 2107-2113 (1972).

5. Johnson, H. H., Morlet, J. G. and Trioano, A. R., Hydrogen Crack Initiation and Delayed Failure in Steel, Trans. Met. Soc. AIME 212, 526-541 (1958).

6. Oriani, R. A., Discussion of Embrittlement of 4130 Steel by Low-Pressure Gaseous Hydrogen, Met. Trans. 1, 2346-2347 (1970).

Key words: Brittleness; fractures (materials); gas embrittlement; high strength alloys; microstructures; notch effects; plastic zone; triaxial stresses.

HYDROGEN EMBRITTLEMENT OF METALS
Louthan, Jr., M. R., Caskey, Jr., G. R. Donovan, J. A., and Rawl, Jr., D. E.
(Du Pont de Nemours (E.I.) and Co., Aiken, SC)
Mater. Sci. Eng. 10, 357-368 (December 1972)

The deleterious effects of hydrogen on the tensile properties of metals are caused by the association and movement of hydrogen with dislocations. Hydrogen-dislocation interactions modify plastic deformation processes by stabilizing microcracks, by changing the work hardening rate, and by solid solution hardening. The extent to which such modifications cause embrittlement depends on the properties and defect structure of the uncharged alloy as well as on hydrogen-induced changes in deformation processes. This paper summarizes an investigation of these phenomena.

Comment:

The authors divide hydrogen embrittlement into several categories:

(1) Embrittlement resulting from hydride formation (e.g., zirconium, titanium, and uranium)

(2) Embrittlement resulting from reaction between hydrogen and some impurity or alloy addition in the metal (e.g., $2H + O \rightarrow H_2O$ in copper, and $4H + C \rightarrow CH_4$ in steel)

(3) Embrittlement resulting from hydrogen which is adsorbed on or absorbed in the metal (surface cracking of 304L when tested in hydrogen and reversible embrittlement of steel).

Other investigators list, as a fourth category, hydrogen blistering or cracking that is caused by the sudden decrease in solubility during cooling of hydrogen-saturated specimens, by prolonged cathodic charging, and by other techniques which produce high pressure gas bubbles. This last-named form of embrittlement is clearly due to gas pressure buildup at microcracks and voids.

The authors indicate that the fact that hydrogen is involved is incidental to the phenomenon. It appears more likely that the phenomenon is related to the rapid decrease in the solubility as a function of temperature exhibited by hydrogen. In several alloy systems this is a step function decrease in solubility which at the proper set of conditions, including low strength at high temperatures, leads to the blister phenomenon.

Hydride embrittlement and embrittlement by hydrogen reaction are reasonably well understood; however, despite a large concentration of effort directed to understanding embrittlement resulting from adsorbed and/or absorbed hydrogen, there is little agreement among investigators. At least three proposed embrittlement mechanisms have received some support:

(1) Lowering of surface energy by adsorption of hydrogen

(2) Decrease of binding energy by interaction of hydrogen with d shell electrons

(3) Internal gas pressure buildup because of hydrogen precipitation at internal voids.

The authors present a phenomenological description of hydrogen embrittlement from analyses of tensile strength and hydrogen uptake and release data for a variety of metals and alloys. A mechanistic interpretation of the data is given; however, no correlation of these observations is made with the above proposed mechanisms. The authors' assertions with respect to the work of other investigators is documented by reference.

The authors conclude that the deleterious effects of hydrogen on the tensile properties of metals are caused by absorbed hydrogen. Enhanced absorption and localized high hydrogen concentrations are caused by hydrogen dislocation interactions which also modify plastic deformation processes by stabilizing microcracks, by changing the work hardening rate, and by solid solution hardening. Embrittlement is promoted by high hydrogen solubility, low stacking fault energies (coplanar dislocation motion) and high yield strengths.

Important References:

1. Fast, V. D., Interaction of Metals and Gases, Academic Press, 54ff (1965).

2. Weiner, L. C., Kinetics and Mechanism of Hydrogen Attack on Steel, Corrosion 17, 137-143 (1961).

3. Vennett, R. M. and Ansell, G. S., Effect of High-Pressure Hydrogen Upon Tensile Properties and Fracture Behavior of 304L Stainless Steel, Trans. ASM 60, 242-251 (June 1967).

4. Barth, C. F. and Steigerwald, E. A., Evaluation of Hydrogen Embrittlement Mechanisms, Met. Trans. 1, 3451-3455 (December 1970).

5. Holzworth, M. L. and Louthan, Jr., M. R., Hydrogen-Induced Phase Transformations in Type 304L Stainless Steels, Corrosion 24, 110-124 (April 1968).

6. Westlake, D. G., A Generalized Model for Hydrogen Embrittlement, Trans. ASM 62, No. 4, 1000-1006 (1969).

7. Williams, D. P. and Nelson, H. G., Embrittlement of 4130 Steel by Low-Pressure Gaseous Hydrogen, Met. Trans. 1, 63-68 (January 1970).

8. Tetelman, A. S., The Mechanism of Hydrogen Embrittlement in Steel, in Fundamental Aspects of Stress Corrosion Cracking, 446-460, NACE (1969).

9. Troiano, A. R., The Role of Hydrogen and Other Interstitials in the Mechanical Behavior of Metals, Trans. ASM 52, 54ff. (1960).

Key words: Absorption; adsorption; deformation; dislocations (materials); hydrogen embrittlement; hydrogen reaction embrittlement; metallic materials; tensile properties; ultimate strength; yield strength.

THE KINETIC AND MECHANICAL ASPECTS OF HYDROGEN-INDUCED FAILURE IN METALS
Nelson, H. G. (California Univ., Los Angeles)
NASA-TN-D-6691 (April 1972)

An experimental and theoretical study was conducted into the kinetic and mechanical aspects of hydrogen-induced failure of metals. Premature hydrogen-induced failure observed to occur in many metal systems involves three stages of fracture: (1) crack initiation; (2) stable slow crack growth; and (3) unstable rapid crack growth. The pressure of hydrogen at some critical location on the metal surface or within the metal lattice has been shown to influence one or both of the first two stages of brittle fracture but has a negligible effect on the unstable rapid crack growth stage. The relative influence of the applied parameters of time, temperature, etc., on the propensity of a metal to exhibit hydrogen-induced premature failure is discussed in detail.

Comment:

Nelson in this NASA TN reports on an extensive study, including a literature review of hydrogen induced cracking. His observations pertaining to the first two stages (crack initiation and slow stable crack growth) are important to future plans for the life prediction for a structure. He presents a large amount of data which needs to be further expanded and correlated for predictive purposes.

Important References:

1. Haynes, R. and Maddocks, P. J., Hydrogen Embrittlement of Titanium, J. Met. Sci. 3, 190-195 (1969).

2. Shupe, D. S. and Stickney, R. B., Thermodynamics of the Solubility and Permeation of Hydrogen in Metals at High Temperature and Low Pressure, J. Chem. Phys. 51, 1620-1625 (August 1969).

3. Hofmann, W. and Rauls, W., Ductility of Steel Under the Influence of External High Pressure Hydrogen, Weld. J. Res. Supp. 44, 225S-230S (May 1965).

4. Wayman, M. L. and Smith, G. C., The Effects of Hydrogen on the Deformation and Fracture of Nickel-Iron Alloys, Acta Met. 19, 227-231 (1971).

5. Holzworth, M. L., Hydrogen Embrittlement of Type 304L Stainless Steel, Corrosion 25, 107-115 (March 1969).

6. Vennett, R. M. and Ansell, G. S., The Effect of High-Pressure Hydrogen Upon the Tensile Properties and Fracture Behavior of 304L Stainless Steel, Trans. ASM 60, 252-251 (1967).

Key words: Brittle fracture; crack initiation; crack propagation; failures (materials); fatigue (materials); hydrogen embrittlement; metallic materials; stainless steels; stress corrosion.

RECENT DEVELOPMENTS IN CLASSICAL (INTERNAL) HYDROGEN EMBRITTLEMENT
Tetelman, A. S. (California Univ., Los Angeles)
Proc. Int. Conf. Effects of Hydrogen on Material Properties and Selection and Structural Design, Champion, PA (23-27 September 1973).

Recent work on gaseous hydrogen embrittlement indicates that classical hydrogen embrittlement results from a combination of two effects: a lowering of the lattice cohesion and a build-up of high internal pressure in microcracks. The former effect results from the endothermic solubility of hydrogen in alpha iron, and is the dominant cause of embrittlement at low hydrogen concentrations. The pressure effect dominates when the hydrogen concentration is high, of the order of 1 to 2 ppm or greater. Both mechanisms can cause discontinuous bursts of crack growth prior to instability. The rate of crack growth is dependent on diffusion rate of hydrogen. Models for discontinuous crack growth are discussed and compared with experimental observations.

Comment:

This paper was one of the overview papers at the 1973 international hydrogen meeting and is a good review of the state-of-the-art at that time. Tetelman discusses the several theories and shows the areas of their applicability, in particular, his decohesion postulation.

Important References:

1. Tetelman, A. S., The Mechanism of Hydrogen Embrittlement in Steel, in Fundamental Aspects of Stress Corrosion Cracking, NACE, 446-460 (1969).

2. Troiano, A. R., Embrittlement of Hydrogen and Other Interstitials, Trans. ASM 52, 54 (1960).

3. Tetelman, A. S. and Robertson, W. D., The Mechanism of Hydrogen Embrittlement Observed in Iron-Silicon Single Crystals, Trans. AIME 224, 775-783 (1962).

4. Sandoz, G., A Unified Theory for Some Effects of Hydrogen Source, Alloying Elements, and Potential on Crack Growth in Martensitic AISI 4340 Steel, Met. Trans. 3, 1169-1176 (1972).

5. Dunegan, H. L. and Tetelman, A. S., Nondestructive Characterization of Hydrogen-Embrittlement Cracking by Acoustic Emission Techniques, Eng. Fract. Mech. 2, 387-402 (1971).

Key words: Crack initiation; elongation; fractures (materials); hydrogen charging; hydrogen embrittlement; lattice diffusion; notch tests; stress intensity factor; tensile tests.

TESTING FOR HYDROGEN ENVIRONMENT EMBRITTLEMENT: EXPERIMENTAL VARIABLES
Gray, H. H. (National Aeronautics and Space Administration, Lewis Research Center, Cleveland, OH)
Hydrogen Embrittlement Testing, ASTM STP-543, 133-151 (L974).

Hydrogen embrittlement is classified into three types: (1) internal reversible hydrogen embrittlement; (2) hydrogen reaction embrittlement; and (3) 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, gas 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.

Comment:

This paper reviews the aspects of testing for hydrogen effects in metals. The various effects of test technique are adeautely covered and this paper is a must for anyone considering any type of testing for the mechanical properties of materials in an environment containing hydrogen.

Important References:

1. 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 TN-D-1453 (December 1962).

2. Nelson, H. G., Williams, D. P. and Tetelman, A. S., Embrittlement of Ferrous Alloy in a Partially Dissociated Hydrogen Environment, Met. Trans. 2, No. 4, 953-959 (April 1971).

3. Walter, R. J., Hayes, H. G. and Chandler, W. T., Influence of Gaseous Hydrogen on Metals, NASA CR-119917 (May 1971).

4. Jewett, R. P., Walter, R. J., Chandler, W. T. and Frohmberg, R. P., Hydrogen Environment Embrittlement of Metals, NASA CR-2163 (1973).

5. Walter, R. J., Jewett, R. P. and Chandler, W. T., On the Mechanism of Hydrogen Environment Embrittlement of Iron- and Nickel-Base Alloys, Mater. Sci. Eng. 5, No. 2, 98-110 (January 1970).

6. Groeneveld, T. P., Fletcher, E. F. and Elsea, A. R., A Study of Hydrogen Embrittlement of Various Alloys, NASA CR-77374 (June 1966).

Key Words: Environmental tests; hydrogen environment embrittlement; hydrogen reaction embrittlement; notch tests; strain rate; test procedures.

TESTING FOR HYDROGEN EMBRITTLEMENT: PRIMARY AND SECONDARY INFLUENCES
Nelson, H. G. (National Aeronautics and Space Administration, Ames Research Center, Moffett Field, CA)
Hydrogen Embrittlement Testing, ASTM STP-543, 152-169 (1974).

An overview of the hydrogen embrittlement process, both internal and external, is presented in an effort to make more clear the type of parameters that must be considered in the selection of a test method and test procedure such that the resulting data may be meaningfully applied to real engineering structures. What are believed to be the three primary influences on the embrittlement process are considered: (1) the original location and form of hydrogen; (2) the transport reactions involved in the transport of hydrogen from its origin to some point where it can interact with the metal to cause embrittlement; and (3) the embrittlement interaction itself. Additionally, a few of the large number of secondary influences on the embrittlement process are discussed. For example, the influence of impurity species in the environment, surface hydride films, and surface oxide films. Specific test procedures are discussed in order to elucidate the parameters which must be considered in the development of a standard test method.

Comment:

This paper supplements Gray's paper (see above) and is an important contribution as a description of the difficulties of testing for hydrogen embrittlement. Both papers should be considered as basic in any future discussions of standard test methods.

Important References:

1. Nelson, H. G., The Kinetic and Mechanical Aspects of Hydrogen-Induced Failure in Metals, NASA TN-D-6691 (April 1972).

2. Tetelman, A. S., The Mechanism of Hydrogen Embrittlement in Steel, in Fundamental Aspects of Stress Corrosion Cracking, NACE, 446-460 (1969).

3. Williams, D. P. and Nelson, H. G., Embrittlement of 4130 Steel by Low-Pressure Gaseous Hydrogen, Met. Trans. 1, 63-68 (January 1970).

4. Oriani, R. A., Hydrogen in Metals, in Fundamental Aspects of Stress Corrosion Cracking, NACE, Houston, TX, 32-49 (1969).

5. Nelson, H. G., Williams, D. P., and Tetelman, A. S., Embrittlement of a Ferrous Alloy in a Partially Dissociated Hydrogen Environment, Met. Trans. 2, 953-959 (April 1971).

Key words: Crack propagation; chemical reactions; embrittlement; environment effects; hydrogen environment embrittlement; material defects; structural stability; test procedures.

ALLOY DESIGN TO RESIST HYDROGEN EMBRITTLEMENT

Bernstein, I. M., and Thompson, A. W. (Carnegie-Mellon Univ., Pittsburgh, PA: Rockwell International Science Center, Thousand Oaks, CA)

Unpublished. To be a chapter in Strengthening Mechanisms and Alloy Design, J. K. Tien, and G. S. Ansell, Eds., to be published by Academic Press.

The behavior of steel, titanium, aluminum, and nickel alloys are analyzed in terms of the specific interrelationships between the metallurgical variables and the susceptibility towards hydrogen embrittlement. It is demonstrated that specific recommendations can be made which should improve the performance of a given material in a hydrogen-bearing or -producing environment. These recommendations are balanced with nonenvironmental strength and toughness constraints, since little progress would be made, for example, by changing and alloying from hydrogen-embrittlement-critical to toughness-critical in a given design environment.

Comment:

The authors have approached alloy design in an almost enclyopedic manner by listing the basic alloy systems. For each system they discuss the relationships between the mechanical properties and hydrogen as reported in the literature in this extensively referenced paper. They present a convincing discussion for the inter-relationship of hydrogen influenced behavior and specific alloy additions. Much more work needs to be done in this area including possible computer analysis of the multitude of information to result in rational alloy design to optimize various properties as required.

Important References:

1. Staehle, R. W., Theory of Stress Corrosion Cracking in Alloys, 223-286, J. C. Scully, Ed., NATO, Brussels (1971).

2. Bernstein, I. M. and Thompson, A. W., Eds., Hydrogen in Metals, ASM. Metals Park, OH (1974).

3. Jewett, R. P., Walter, R. J., Chandler, W. T., and Frohmberg, R. P., Hydrogen Environment Embrittlement of Metals, NASA CR-2163 (1973).

4. Brown, B. F., Ed., Stress Corrosion Cracking in High Strength Steels and in Aluminum and Titanium Alloys, Naval Research Lab., Washington, D. C. (1972).

5. Green, J. A. S. and Montague, W. G., Observations on the SCC of an Al-5% Zn-2.5Mg. Ternary and Various Quanternary Alloys; 1st Technical Report to ONR, Martin Marietta Corp., Baltimore, MD (August 1974).

6. Latanision, R. M. and Opperhauser, H., Further Observations on the Effect of Grain Boundary Segregation in the Hydrogen Embrittlement of Nickel, MMC-TP-74-17C. Martin Marietta Corp., Baltimore, MD (July 1974).

Key words: Aluminum alloys; cracking (fracturing); design criteria; ductility; embrittlement; failures (materials); hydrogen; metallography; microstructures; nickel alloys; titanium alloys.

A UNIFIED THEORY FOR SOME EFFECTS OF HYDROGEN SOURCE, ALLOYING ELEMENTS, AND POTENTIAL ON CRACK GROWTH IN MARTENSITIC AISI 4340 STEEL
Sandoz, G. (Naval Research Lab., Washington, DC)
Met. Trans. 3, 1169 - 1176 (May 1972).

The effects of hydrogen on crack growth in martensitic AISI 4340 steel are shown to be fundamentally the same whether the hydrogen is supplied as molecular gas, through stress corrosion, or by electrolytic charging. This was based on the observation that at equal values of threshold stress intensity, hydrogen from the several sources produced identical fractographic crack growth mode. It is shown that the values of threshold stress intensity produced by hydrogen from the various sources fall within an upper bound produced by molecular hydrogen gas, and a lower bound produced by cathodic charging. Changing concentrations of carbon or maganese in the steel at a fixed yield strength produced effects during SCC similar to those produced by anodic or cathodic polarization.

Comment:

This paper presents evidence that the hydrogen effects on high strength steel (in this case martenitic 4340) are independent of hydrogen source. This is important because it leads to the conclusion that in this material the driving force and rate controlling factors are internal to the material.

Important References:

1. Farrell, K., Cathodic Hydrogen Absorption and Severe Embrittlement in a High Strength Steel, Corrosion 26, No. 3, 105-110 (March 1970).

2. Beachem, C. D., A New Model for Hydrogen-Assisted Cracking (Hydrogen Embrittlement), Met. Trans. 3, 437-451 (February 1972).

3. Barth, C. F. and Steigerwald, E. A., Evaluation of Hydrogen Embrittlement Mechanics, Met. Trans. 1, 3451-3455 (December 1970).

4. Sandoz, G., Effects of Alloying Elements on the Susceptibility to Stress Corrosion Cracking of Martensitic Steels in Salt Water, Met. Trans. 2, No. 4, 1055-1063 (April 1971).

5. Brown, B. F., Stress-Corrosion Cracking: A Perspective View of the Problem, NRL Report 7130 (AD-711589) (16 June 1970).

6. Campbell, J. E., Effects of Hydrogen Gas on Metals at Ambient Temperature, DMIC Report S-31, Battelle Memorial Institute (April 1970).

Key words: Cathodic polarization; chemical composition; crack propagation; gas embrittlement; hydrogen charging; martensite; material degradation; stress corrosion.

II - TYPES OF HYDROGEN EMBRITTLEMENT AND RELATED EFFECTS

EVALUATION OF HYDROGEN EMBRITTLEMENT MECHANISMS
Barth, C. F. and Steigerwald, E. A. (TRW Equipment Labs., Cleveland, OH)
Met. Trans. 1, 3451-3455 (December 1970).

The incubation time which precedes the initiation of slow crack growth in the delayed failure of high-strength steel containing hydrogen was reversible with respect to the applied stress. The kinetics of the reversibility process indicated that it was controlled by the diffusion of hydrogen and had an activation energy of approximately 9000 cal per mole. Reversible hydrogen embrittlement studies were also conducted at liquid nitrogen temperatures where diffusion processes should not occur. The previously reported low temperature embrittlement behavior was confirmed indicating a basic interaction between hydrogen and the lattice. The experimental results could be satisfactorily explained by the lattice embrittlement theory proposed by Troiano.

Important References:

1. Williams, D. P. and Nelson, H. G., Embrittlement of 4130 Steel by Low-Pressure Hydrogen, Met. Trans. 1, 63-68 (January 1970).

2. Sturges, C. M. and Miodownik, A. P., The Interaction of Hydrogen and Dislocations in Iron, Acta Met. 17, 1197-1207 (September 1969).

Key words: Crack propagation; diffusion; embrittlement; failures (materials); high strength steels; hydrogen; material degradation.

EMBRITTLEMENT BY INTERNAL AND BY EXTERNAL HYDROGEN
Van Leeuwen, H. P. (National Aerospace Lab., Amsterdam, Netherlands)
Corrosion 31, No. 5, 154-159 (May 1975).

By use of equations developed by the author, hydrogen pressures are calculated in nascent microcracks producing delayed failure. The results suggest a high degree of similarity between internal cracking due to dissolved hydrogen and external cracking due to environmental molecular hydrogen. This supports the surface adsorption and lattice decohesion models of hydrogen embrittlement rather than the planar pressure theory. The latter may be applicable under extreme charging conditions leading to blistering and cracking in the absence of an applied stress, especially at elevated temperatures.

Comment:

The author develops his equations based on models of voids in the grain boundary. The pressure is developed through an application of an extension of Sieverts Law. This type of theoretical approach is extremely useful in helping to explain the behavior but must be tempered by experimental results and critical experiments which are yet to be reported.

Important References:

1. Van Leeuwen, H. P., A Quantitative Model of Hydrogen Induced Grain Boundary Cracking, Corrosion 29, No. 5, 197-204 (May 1973).

2. Williams, D. P. and Nelson, H. G., Embrittlement of 4130 Steel by Low-Pressure Gaseous Hydrogen, Met. Trans. 1, 63-68 (January 1970).

3. Liu, H. W., Stress-Corrosion Cracking and the Interaction Between Crack-Tip Stress Field and Solute Atoms, J. Basic Eng. 92, 633 (September 1970).

4. Oriano, R. A., Hydrogen in Metals, in Fundamental Aspects of Stress Corrosion Cracking, NACE-1, 32 (1969).

5. St. John, C. and Gerberich, W. W., The Effect of Loading Mode on Hydrogen Embrittlement, Met. Trans. 4, 589 (February 1973).

Key words: Cracks; failures (materials); environment effects; hydrogen charging; hydrogen environment embrittlement; material degradation; microstructures.

A MECHANISM FOR THE EMBRITTLEMENT OF HIGH-STRENGTH STEELS BY AQUEOUS ENVIRONMENTS
Hanna, G. L., Troiano, A. R., and Steigerwald, E. A. (TRW Equipment Labs., Cleveland, OH and Case Inst. of Tech., Cleveland, OH)
ASM Trans. Quart. 57, No. 3, 658-671 (September 1964).

Environmentally-induced crack propagation was studied in steels with particular emphasis on the influence of aqueous media. Low alloy martensitic steels, 4340 and 300M, were susceptible to delayed failure in water or moist air environment. Constant-load, stress-rupture tests on precracked specimens of 4340 and 300M steels indicated that less than 1 grain of water per cubic foot of gas induced delayed failure. The effects of notch sensitivity, the oxygen content of water, cathodic polarization, and applied stress were examined with the specific purpose of defining the mechanism which governed the embrittlement. The results, particularly the reversibility of the incubation time required to initiate discontinuous crack growth, indicated that hydrogen produced by the corrosion process was the primary cause of the embrittlement.

Important References:

1. Barnett, W. J. and Troiano, A. R., Crack Propagation in Hydrogen Induced Brittle Fracture of Steel, Trans. AIME 209, 486 (1959).

2. Johnson, H. H., Morlet, J. G. and Troiano, A. R., Hydrogen, Crack Initiation, and Delayed Failure in Steel, Trans. AIME 212, 528 (August 1958).

Key words: Cathodic polarization; contaminants; crack initiation; environment effects; high strength steels; hydrogen embrittlement; material degradation; notch effects; stresses.

EFFECT OF HYDROGEN ON HIGH STRENGTH AND MARTENSITIC STEELS
Gerberich, W. W. (Minnesota, Univ., Minneapolis)
Proc. Int. Conf. Effects of Hydrogen on Material Properties and Selection and Structural Design, Champion, PA
(23-27 September 1973)

The equilibrium and kinetic models for threshold and crack growth conditions were found to be consistent with available data on high strength steels. It was shown with reasonable certainty that: (1) thresholds can be predicted based upon yield strength, concentration level and stress field variables - increasing these variables decreases the threshold; (2) thresholds can be predicted under relatively plane stress and plane strain conditions - increasing plate thickness decreases the threshold; (3) Stage I, II and III crack growth rate observations can be explained on the basis of the hydrogen stress field interaction and the type of microscopic growth process; (4) extremes of plane stress and plane strain growth kinetics are due to large differences in the pressure tensor gradient. It has been hypothesized but with less certainty that: (1) the effect of alloying elements on the threshold are generally small - secondary effects are due to their influence on yield strength or initial hydrogen concentration levels; (2) the effect of tempering temperature on threshold is only a yield strength effect - increased tempering temperatures produce higher thresholds; (3) the main effect of environment is to control the availability of atomic hydrogen at the crack tip; (4) tempering, aging and alloying parameters affect crack growth rate by controlling hydrogen trapping and yield strength. Alloy additions, which provide trap sites, may decrease kinetics by three orders of magnitude. Careful kinetic analyses of different alloying systems under varying experimental conditions must precede development of more accurate theoretical models.

Important References:

1. Steigerwald, E. A., Schaller, F. W. and Troiano, A. R., Doscontinuous Crack Growth in Hydrogenated Steel, Trans. AIME 215, 1048-1052 (1959).

2. Benjamin, W. D. and Steigerwald, E. A., Effect of Composition on the Environmentally Induced Delayed Failure of Precracked High Strength Steel, Met. Trans. 2, 606-608 (1971).

3. Beachem, C. D., A New Model for Hydrogen Assisted Cracking (Hydrogen Embrittlement), Met. Trans. 3, 437-451 (1972).

4. Farrell, K. and Quarrell, A. G., Hydrogen Embrittlement of an Ultrahigh Tensile Steel, J. Iron Steel Inst. 202, 1002-1011 (1964).

5. Kim, C. D. and Loginow, A. W., Techniques for Investigating Hydrogen-Induced Cracking of Steels with High Yield Strength, Corrosion 24, No. 1, 313-318 (1968).

6. Kerns, G. E. and Staehle, R. W., Slow Crack Growth of High Strength Steel in Chlorine and Hydrogen Halide Gas Environments, Scripta Met. 6, 1189-1194 (1972).

Key words: Crack growth rate; crack propagation; diffusion; embrittlement; fractures (materials); high strength alloys; high strength steels; martensite; plane strain; plane stress; stress intensity factor; yield strength.

DUCTILITY OF STEEL UNDER INFLUENCE OF EXTERNAL HIGH PRESSURE HYDROGEN
Hofmann, W. and Rauls, W. (Institute for Materials of Construction and Welding of the Technical Univ. of Braunschweig, West Germany)
Weld. J. Res. Supp. 44, No. 5, 225S-230S (May 1965).

The authors describe the results of an experiment in which an external pressure of about 100 atm is used to cause embrittlement. Most tests were performed on a carbon steel. It was determined that under the influence of external high pressure hydrogen steel loses some tensile ductility. In deformation oxide-free regions are produced which then absorb atomic hydrogen. Cracks caused by hydrogen form only during the high stress phase of tensile testing and only if hydrogen is available during plastic deformation.

Important References:

1. Troiano, A. R., The Role of Hydrogen and Other Interstitials in the Mechanical Behavior of Metals, Trans. ASM 52, 54 (1960).

2. Hofmann, W. and Vibrans, G., Rev. Metallurg. 57, No. 2, 88-90 (1960).

3. Hofmann, W., Rauls, W. and Vogt, J., Acta Met. 10, No. 7, 688-690 (1962).

Key words: Carbon steels; deformation; ductility; environment effects; high pressure; high temperature; hydrogen; tensile strength.

HYDROGEN GAS EMBRITTLEMENT

Johnson, H. H. (Cornell Univ., Ithaca, NY)

Proc. Int. Conf. Effects of Hydrogen on Material Properties and Selection and Structural Design, Champion, PA (23-27 September 1973).

It has been established in the past decade that external hydrogen gas causes brittleness in many alloy systems including titanium and titanium alloys, and nickel and nickel-base alloys. Hydrogen pressures from much less than 1 atm (10^5 N/m^2) to 10,000 psi (6.8×10^7 N/m^2) have been used, and it is clear that in general susceptibility to hydrogen gas increases with pressure. Parameters measured as indices of brittleness include elongation, reduction of area, notch tensile strength, time to failure, crack growth rate, threshold stress and threshold stress intensity. In common with classical hydrogen brittleness, the notch and flaw-associated properties are far more sensitive to hydrogen gas than are the unnotched properties, and brittleness is more evident in high strength alloys than low strength alloys. The analysis suggests that brittleness may result whenever material under very high stress is exposed to hydrogen. In high strength materials very high local stresses may be expected because of the complex micro-structures associated with high strength levels. In lower strength materials plastic deformation may be expected to intervene before very high local stresses are developed. This suggests that whiskers of metals normally soft in bulk form might well be brittle in the presence of hydrogen gas, since very high stresses may be attained in whiskers. It also suggests that experimental studies of the interaction between hydrogen and unstressed material will not provide information directly relevant to hydrogen brittleness.

(FOR LISTING OF IMPORTANT REFERENCES, KEY WORDS AND A DUPLICATE ABSTRACT, SEE PAGE 13).

EMBRITTLEMENT OF A FERROUS ALLOY IN A PARTIALLY DISSOCIATED HYDROGEN ENVIRONMENT

Nelson, H. G., Williams, D. P., and Tetelman, A. S. (National Aeronautics and Space Administration, Ames Research Center, Moffett Field, CA; California Univ., Los Angeles)

Met. Trans. 2, 953-959 (April 1971).

Gaseous hydrogen embrittlement of quenched and tempered 4130 steel was studied as a function of temperature from -42°C to 164°C in a partially dissociated hydrogen environment at low molecular hydrogen pressures (0.0008 torr.). The presence of atomic hydrogen was found to increase the rate of hydrogen-induced, slow crack growth by several orders of magnitude and to significantly alter the temperature dependence of embrittlement from what is observed in the presence of molecular hydrogen alone. Based on a previous study, these observations are interpreted in terms of a difference between the hydrogen-transport reaction step controlling hydrogen-induced slow crack growth in the molecular hydrogen and the atomic-molecular hydrogen environments. Finally a comparison is made between the kinetics of hydrogen-induced, slow crack growth observed in the presence of atomic molecular hydrogen and the kinetics of known, possible hydrogen-transport reactions in an effort to identify the reaction step controlling hydrogen embrittlement in the presence of atomic hydrogen.

Important References:

1. Tetelman, A. S., The Mechanism of Hydrogen Embrittlement, in Fundamental Aspects of Stress Corrosion Cracking, NACE, 446-460 (1969).

2. Johnson, H. H., On Hydrogen Brittleness in High Strength Steels, in Fundamental Aspects of Stress Corrosion Cracking, NACE, 439-445 (1969).

3. Williams, D. P. and Nelson, H. G., Embrittlement of 4130 Steel by Low-Pressure Gaseous Hydrogen, Met. Trans. 1, 63-68 (1970).

4. Walter, R. J. and Chandler, W. T., Effect of High-Pressure Hydrogen on Metals, Paper D8-14.2, ASM Fall Meeting, Detroit, MI (October 1968).

Key words: Embrittlement; failure mecahnisms; gas embrittlement; high strength steels; hydrogen; hydrogen environment embrittlement; material degradation; temperature effects.

EMBRITTLEMENT OF 4130 STEEL BY LOW-PRESSURE GASEOUS HYDROGEN
Williams, D. P. and Nelson, H. G. (National Aeronautics and Space Administration, Ames Research Center, Moffett Field, CA)
Met. Trans. 1, 63-68 (January 1970),

A study has been made of fully hardened 4130 steel in low-pressure, <760 torr, gaseous hydrogen. It was found that the embrittlement was caused by hydrogen-induced, slow crack growth. In the range of temperature from 80°C to 25°C, the crack growth rate increased with decrease in temperature; in the range from 0°C to -80°C, the rate decreased with decrease in temperature. It was also found that the crack growth rate had a different pressure dependence at high temperatures than at low temperatures. From a consideration of these experimental data, as well as from data from earlier investigations, it was determined that gaseous hydrogen embrittlement and the embrittlement of hydrogen-charged steels are basically the same phenomenon. The data are discussed in terms of a surface reaction model that adequately explains both gaseous hydrogen embrittlement and the embrittlement of hydrogen charged steels.

Comment:

It appears that the authors' assertion that based on the experimental effort gaseous hydrogen embrittlement and the embrittlement of hydrogen charged steel are basically the same phenomenon and are adequately explained by a surface reaction phenomenon is a bit premature. Work needs to be done on other alloy systems over a greater range of temperatures and pressures.

Important References:

1. Walter, R. J. and Chandler, W. T., Effect of High-Pressure Hydrogen on Storage Vessel Materials, Rocketdyne Report No. R-6851 (January 1967).

2. Tetelman, A. S., The Mechanism of Hydrogen Embrittlement in Steel, in Fundamental Aspects of Stress Corrosion-Cracking, NACE, 446-460 (1969).

3. Oriani, R. A., Hydrogen in Metals, in Fundamental Aspects of Stress Corrosion Cracking, NACE, 32-49 (1969).

Key words: Crack growth rate; crack propagation; environment effects; failures (materials); gas embrittlement; high strength steels; hydrogen charging; hydrogen environment embrittlement; material degradation; temperature effects.

HYDROGEN ENVIRONMENT EMBRITTLEMENT OF METALS
Jewett, R. P., Walter, R. J., Chandler, W. T., and Frohmberg, R. P. (Rocketdyne, Canoga Park, CA)
NASA CR-2163 (March 1973).

A wide variety of pure metals and alloys have been found to be susceptible to hydrogen environment embrittlement. Elastic properties, yield strength, and, in many cases, the ultimate tensile strength are not affected by the hydrogen environment. The most significant effects of the hydrogen environment are on tensile ductility, notch strength, and crack behavior. Four categories of embrittlement, based on the results of tensile tests conducted in 10,000 psig hydrogen, have been established for classifying this susceptibility of metals to hydrogen environment embrittlement: (1) extreme embrittlement, large decrease of notch strength and ductility (high strength steels and high-strength nickel-base alloys are in this category); (2) severe embrittlement, considerable decrease of notch strength and ductility (the majority of the metals tested were in this category, including ductile lower-strength steels, Armco steel, pure nickel, and titanium-base alloys); (3) slight embrittlement, small decrease in notch strength and little or no decrease in ductility (the nonstable AISI Type 300 series stainless steels, beryllium-copper, and commercially pure titanium are in this category); (4) negligible embrittlement (the aluminum alloys, stable austenitic stainless steels, A-286, and OFHC copper are in this category). The effects of hydrogen environments on the tensile properties of metals have been investigated as a function of deformation rate, hydrogen pressure, notch severity, exposure time in hydrogen, temperature, and weldments. Hydrogen can increase the sustained as well as cyclic crack growth rate. Two methods for the prevention of hydrogen environment embrittlement are the use of protective coatings and the addition of inhibitors to hydrogen. Metallographic studies have shown that fracture initiation in high-pressure hydrogen occurs at the metal surface. The mechanism by which gaseous hydrogen embrittles metals has not been established.

Comment:

This excellent report contains extensive amounts of data and wisely refrains from postulating a specific mechanism. The data presented in this report are worth additional analysis.

Important References:

1. Troiano, A. R., The Role of Hydrogen and Other Interstitials in the Mechanical Behavior of Metals, Trans. ASM 52, 54 (1960).

2. Walter, R. J. and Chandler, W. T., Effects of High Pressure Hydrogen on Metals at Ambient Temperature, Rocketdyne Report R-7780-1, -2, -3 (1969).

3. Williams, D. P. and Nelson, H. G., Embrittlement of 4130 Steel by Low-Pressure Gaseous Hydrogen, Met. Trans. 1, 63-68 (1970).

4. Walter, R. J., Jewett, R. P., and Chandler, W. T., On The Mechanism of Hydrogen-Environment Embrittlement of Iron- and Nickel-base Alloys, Mater. Sci. Eng. 5, 98-110 (1969/1970).

5. Groenveld, T. P., Fletcher, E. E., and Elsea, A. R., A Study of Hydrogen Embrittlement of Various Alloys, Summary Report, Contract NAS 8-20029 (1966).

6. Walter, R. J., Hayes, H. G., and Chandler, W. T., Mechanical Properties of Inconel 718, Waspaloy, A-286, and Ti-5Al-2.5Sn ELI in Pure Gaseous H_2, Rocketdyne Report R-8187 (April 1970).

7. Chandler, W. T. and Walter, R. J., Hydrogen Effects in Refractory Metals and Alloys, in Refractory Metals and Alloys, Plenum Press, 197 (1968).

8. Hofmann, W. and Rauls, W., Ductility of Steel Under Influence of External High Pressure Hydrogen, Weld. J. Res. Supp. 44, No. 5, 225S-230S (May 1965).

9. Vennett, R. M. and Ansell, G. S., Effect of High-Pressure Hydrogen Upon Tensile Properties and Fracture Behavior of 304L Stainless Steel, Trans. ASM 60, 242-251 (June 1967).

10. 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 TN-D-1453 (December 1962).

11. Nelson, H. G., Williams, D. P. and Tetelman, A. S., Embrittlement of Ferrous Alloy in a Partially Disassociated Hydrogen Environment, Met. Trans. 2, No. 4, 953-959 (April 1971).

Key words: Brittle fractures; crack initiation; crack propagation; fractures (materials); gas embrittlement; hydrogen environment embrittlement; metallic materials; safety factors; safety criteria.

ON THE MECHANISM OF HYDROGEN-ENVIRONMENT EMBRITTLEMENT OF IRON- AND NICKEL-BASE ALLOYS

Walter, R. J., Jewett, R. P., and Chandler, W. T. (Rocketdyne, Canoga Park, CA)
Mater. Sci. Eng. 5, 98-110 (1969/1970).

The literature on internal hydrogen embrittlement and hydrogen-environment embrittlement of iron-base and nickel-base alloys, with emphasis on the mechanisms by which embrittlement occurs, is reviewed. In general, there is little correlation between susceptibilities of various metals to internal hydrogen embrittlement and hydrogen-environment embrittlement.

Hydrogen-environment embrittlement involves crack initiation at the metal surface while internal hydrogen embrittlement involves crack initiation inside the metal. Two surface-dependent mechanisms for hydrogen-environment embrittlement are proposed. One is based upon the heat of adsorption of hydrogen, which decreases the strain energy needed to initiate a crack. The second mechanism is the absorption of hydrogen into the surface, where it lowers the surface ductility, possibly by inhibition of dislocation generation at the surface, or by increasing the lattice friction stress for dislocation motion at the surface.

Comment:

This paper is a detailed review of the literature which was followed by the more extensive experimental effort reported in NASA CR-2163. It is interesting to note that the authors were less willing to postulate mechanisms after the experimental effort than after the literature review.

Important References:

1. Groeneveld, T. P., Fletcher, E. E. and Elsea, A. R., Review of Literature on Hydrogen Embrittlement, Special Report on Contract NAS 8-20029 (January 1966).

2. Tetelman, A. S., The Mechanism of Hydrogen Embrittlement in Steel, in Fundamental Aspects of Stress Corrosion Cracking, NACE, 446-460 (1969).

3. Fletcher, E. E., Berry, W. E. and Elsea, A. R., Stress-Corrosion and Hydrogen-Stress Cracking of High Strength Steel, DMIC-232, Battelle Memorial Institute (July 1966).

4. Elsea, A. R. and Fletcher, E. E., Hydrogen-Induced, Delayed, Brittle Failures of High Strength Steels, DMIC-196, Battelle Memorial Institute (January 1964).

5. Walter, R. J. and Chandler, W. T., Effects of High-Pressure Hydrogen on Storage Vessel Materials, ASM Report No. W8-2.4 (1968).

6. Fletcher, E. E. and Elsea, A. R., Hydrogen Movement in Steel - Entry Diffusion, and Elimination, DMIC-219, Battelle Memorial Institute (1965).

7. Lounamaa, K. and Braggstrom, G., Cracking in Hydrogen Charged Tensile Test Specimens, J. Iron and Steel Inst. (London) 203, Pt. 7, 702-706 (1965).

8. Vennett, R. M. and Ansell, G. A., A Study of Gaseous Hydrogen Damage in Austenitic Stainless Steel, Proc. ASTM-ASME-ASM Symp. Effects of Gaseous Hydrogen on Metals, Detroit, MI (1968).

9. Oriani, R. A., Hydrogen in Metals, in Fundamental Aspects of Stress Corrosion Cracking, NACE, 32 (1969).

10. Benson, Jr., R. B., Dann, R. K., and Roberts, Jr., L. W., Hydrogen Embrittlement of Stainless Steels, Trans. AIME 242, No. 10, 2199-2205 (1968).

11. Wilcox, B. A. and Smith, G. C., Intercrystaline Fracture in Hydrogen Charged Nickel, Acta Met. 13, No. 3, 331-343 (1965).

12. Johnson, H. H., On Hydrogen Brittleness in High Strength Steels, in Fundamental Aspects of Stress Corrosion Cracking, NACE, 439 (1969).

Key words: Crack initiation; crack propagation; delayed failure; embrittlement; failure mechanisms; high strength alloys; hydrogen environment embrittlement; iron alloys; nickel alloys; stress intensity factor

IIC - Hydrogen Reaction Embrittlement (HRE)

THE EFFECTS OF HIGH-PRESSURE HIGH-TEMPERATURE HYDROGEN ON STEEL
Fletcher, E. E. and Elsea, A. R. (Battelle Memorial Inst., Columbus, OH)
DMIC Report 202 (March 26, 1964).

This Battelle report describes the deleterious effects of hydrogen gas on steel at elevated temperatures and/or pressures. Factors that determine the degree of attack are temperature, hydrogen partial pressure, stress, exposure time, composition of the steel, and structure of the steel. For a given exposure time, hydrogen attack on steel starts at a limiting temperature and pressure. Longer exposure times permit attack to start at lower temperatures. Also, the higher the temperature, the lower the limiting pressure and vice versa. Prior cold work or creep during exposure accelerates the attack.

Key words: Absorption; chemical reactions; diffusion; ductility; embrittlement; gas embrittlement; high pressure; high temperature; material defects; strain rate.

EFFECT OF TEMPERATURE AND STATE OF STRESS ON HYDROGEN EMBRITTLEMENT OF HIGH STRENGTH STEEL

Greer, J. B., Von Rosenberg, E. L., and Martinez, J. (Esso Production Research Co., Houston, TX)

Corrosion 28, No. 10, 378-384 (1972).

Acidizing is a primary method of oil and gas well completion in carbonate formations and is frequently used as a stimulation technique in the shaley Gulf Coast sands. The question of the effect of acidizing on tubular goods has been of greater interest since the use of high strength materials in deep wells (acidizing depths have ranged to 22,000 feet). The two effects of acid on the steel are: (1) the corrosion and simple metal loss, and (2) embrittlement and catastrophic cracking of the material. Only the second of these is considered in this report.

Comment:

The investigators concluded that: (1) increasing temperature is beneficial in reducing hydrogen embrittlement of high strength steel by 15 percent HCl; (2) pressure, apart from stress considerations, and corrosion are not significant factors in hydrogen embrittlement by 15 percent HCl; and (3) combined stresses are important in embrittlement failure theories. A new theory incorporating the third conclusion is proposed as an addition to the current, commonly accepted theories of hydrogen embrittlement.

Important References:

1. Coulter, A. W. and Claiborne, T. S., Stress Corrosion Cracking of Oil Field Tubing in Aqueous Hydrochloric Acid, Materials Protection 7, 23 (June 1968).

2. Davis, R. A., Stress Corrosion Cracking Investigation of Two Low Alloy High Strength Steels, Corrosion 19, No. 2, 45 (1963).

3. Wayman, M. L. and Smith, G. C., The Hydrogen Embrittlement of Fe-Ni Martensites, Met. Trans. 1, 1189 (May 1970).

4. Dvoracek, L. M., Sulfide Stress Corrosion Cracking of Steels, Corrosion 26, No. 5, 177 (1970).

Key words: Biaxial stress; brittle fractures; corrosion; crack initiation; crack propagation; fracture analysis; high strength steels; hydrogen environment embrittlement; laboratory tests; pipes (tubes); stress analysis; sulfide stress cracking.

HYDROGEN ATTACK ON STEEL
Westphal, D. A. and Worzala, F. J. (Wisconsin Univ., Madison)
Proc. Int. Conf. Effects of Hydrogen on Material Properties and Selection and Structural Design, Champion, PA (23-27 September 1973).

Hydrogen attack of steel is a phenomenon in which methane forms internally, causing swelling of the material and eventual brittle-type failure. It was shown that the incubation time for hydrogen attack varies drastically with exposure temperature and pressure. At temperatures below 200°C either very large hydrogen pressures or very long times are necessary to nucleate fissures or obtain significant volume increase. The duration of the incubation period may be increased by the use of material with larger grain size. The carbon used to produce methane during hydrogen attack comes from solid solution. Carbides are not appreciably affected during the incubation period, although they replenish the carbon in solution during more advanced stages of hydrogen attack. The incubation period is characterized by the nucleation and growth of methane bubbles, as evidenced by transmission electron microscopy. Increasing either exposure temperature or hydrogen pressure increases the rate of bubble growth. Incubation time appears to be related to the growth of methane bubbles since it can be used as a normalizing factor for exposure time and bubble size. During the early part of rapid attack the nucleation of fissures does not involve bubbles within the grains. Rather, it appears that grain boundary bubbles play the major role in the onset of rapid attack.

Important References:

1. Weiner, L. C., Kinetics and Mechanism of Hydrogen Attack of Steel, Corrosion 17, 137-143 (1961).

2. Allen, R. E., Jansen, R. J., Rosenthal, P. C. and Vitovec, F. H., Analysis of Probable Mechanisms of High-Temperature Hydrogen Attack of Steel, Proc. API 42, 452-462 (1962).

3. Vitovec, F. H., Growth Rate of Fissures During Hydrogen Attack of Steels, Proc. API 44, 179-188 (1964).

4. Nelson, R. S., Mazey, D. J., and Barnes, R. S., The Thermal Equilibrium Shape and Size of Holes in Solids, Phil. Mag. 11, 91-111 (1965).

Key words: Brittle fractures; chemical reactions; crack initiation; cracking (fracturing); failure mode; gas embrittlement; grain boundaries; hydrogen reaction embrittlement; microstructures; metallography; static crack growth.

THE KINETIC AND DYNAMIC ASPECTS OF CORROSION FATIGUE IN A GASEOUS HYDROGEN ENVIRONMENT

Nelson, H. G., Tetelman, A. S., and Williams, D. P. (National Aeronautics and Space Administration, Ames Research Center, Moffett Field, CA: California Univ., Los Angeles)

Proc. NACE Conf. Corrosion Fatigue: Chemistry, Mechanics and Microstructure, Connecticut Univ., Storrs, 359-365 (14-18 June 1971).

The purpose of the investigation reported was to study the stable, subcritical crack growth stage of fracture under conditions of corrosion fatigue such that the importance of the kinetic and dynamic aspects of environment-sensitive behavior could be demonstrated. Specifically, consideration was given to a comparison of the cyclic loading of a titanium alloy in a low pressure gaseous hydrogen environment with that in a vacuum. Titanium exhibits a broad range of susceptibility to environmental hydrogen embrittlement, depending on alloy microstructure and rate of loading, and, thus, a variation in these two parameters under conditions of cyclic loading where frequency could be varied was used to dramatize the importance of the kinetic and dynamic aspects of environmental embrittlement as well as establish the corrosion fatigue characteristics of this hydrogen metal system.

Important References:

1. Windle, A. H. and Smith, G. C., The Effect of Hydrogen on the Deformation and Fracture of Polycrystalline Nickel, Metal Sci. J. 4, 136-144 (July 1970).

2. Nelson, H. G., Williams, D. P., and Stein, J. E., Environmental Hydrogen Embrittlement of an α-β Titanium Alloy: Effect of Microstructure, Met. Trans. 3, 369-475 (February 1972).

3. Beck, T. R., Blackburn, M. J., and Speidel, M. O., Stress Corrosion Cracking of Titanium Alloys: SCC of Aluminum Alloys, Polarization of Titanium Alloys in HCl and Correlation of Titanium and Aluminum Behavior, Contract NAS 7-489 Quarterly Progress Report No. 11 (March 1969).

4. Nelson, H. G., Environmental Hydrogen Embrittlement of Titanium - A Qualitative Comparison with Stress Corrosion Cracking, Proc. Conf. Mechanisms of Stress Corrosion Cracking in Titanium, Atlanta (1971).

5. Crooker, T. W., Judy, Jr., R. W. and Cooley, L. A., Subcritical Crack Growth in Several Titanium Alloys, NRL Report 2160 (September 1970).

6. Gallagher, J. P., Corrosion Fatigue Crack Growth Behavior Above and Below K_{ISCC}, NRL Report 7064 (May 1970).

Key words: Corrosion; crack propagation; cracking (fracturing); embrittlement; environment effects; fatigue (materials); gas embrittlement; microstructures; subcritical crack growth; titanium alloys.

ENVIRONMENTAL HYDROGEN EMBRITTLEMENT OF AN $\alpha-\beta$ TITANIUM ALLOY: EFFECT OF MICROSTRUCTURE

Nelson, H. G., Williams, D. P., and Stein, J. E. (National Aeronautics and Space Administration, Ames Research Center, Moffet Field, CA)
Met. Trans. 3, 469-475 (February 1972).

Environmental hydrogen embrittlement of a Ti-6Al-4V alloy has been studied as a function of test displacement rate and of variations in $\alpha-\beta$ microstructure. Embrittlement in low pressure ($\sim$1 atm) gaseous hydrogen was inversely dependent on test displacement rate and strongly dependent on microstructure. At a given displacement rate, microstructures having a continuous α-phase matrix were less severely embrittled than those having a continuous β-phase matrix. Further, brittle fracture occurred in the former microstructures by transgranular cleavage and in the latter microstructures by intergranular separation. These observations are consistent with previous studies made on slow strain-rate embrittlement of hydrogen-charged titanium alloys and are explained in terms of relative hydrogen transport rates within the α-phase and β-phase titanium.

Important References:

1. Livanov, V. A., Kotachev, B. A. and Buhanova, A. A., The Science, Technology and Application of Titanium, Jaffee and Promisel, Eds., Pergamon Press, 561-675 (1970).

2. Johnson, R. E., The Science, Technology and Application of Titanium, Jaffee and Promisel, Eds., Pergamon Press, 1175-1186 (1970).

Key words: Brittle fractures; environment effects; fractures (materials); hydrogen embrittlement; microstructure; titanium alloys.

THE REACTION OF A TITANIUM ALLOY WITH HYDROGEN GAS AT LOW TEMPERATURES
Williams, D. N. and Wood, R. A. (Battelle Memorial Inst., Columbus, OH)
J. Less-Common Metals 31, 239-247 (1973)

An investigation of the effect of temperature on the surface hydriding reaction of Ti-5Al-2.5Sn alloy exposed to hydrogen at 250 psig was made. The temperature range studied extended from 160°F to -160°F. Reaction conditions were controlled so as to expose a vacuum-cleaned, oxide-free alloy surface to an ultra-pure hydrogen atmosphere. Reaction times up to 1548 h were studied.

The hydriding reaction was extremely sensitive to experimental variables and the reproducibility of reaction behavior was poor. However, it was demonstrated that the reaction proceeded quite rapidly at 160°F; as much as 1 mil surface hydriding was observed after exposure for 162 h. The amount of hydriding was observed to decrease with decreasing temperature at 75°F, -36°F, and -76°F. No surface hydriding was detected either by vacuum fusion analysis or by metallographic examination after exposure for 1458 h at -110°F or -160°F. Tensile properties were unaffected by surface hydriding of the severity developed in this program (up to 1 mil thick) as determined by slow strain rate testing of hydrided sheet tensile samples.

Important References:

1. Williams, D. N., Koehl, B. G. and Bartlett, E. S., The Reaction of Titanium with Hydrogen Gas at Ambient Temperatures, J. Less-Common Metals 19, 385 (1969).

2. Wickstrom, W. A. and Etheridge, B. R., Investigation into the Compatibility of Hydrogen and Titanium, Adv. Cryogenic Eng. 13, 334 (1968).

3. Williams, D. N. and Maykuth, D. J., Reaction of Titanium with Gaseous Hydrogen at Ambient Temperatures, DMIC Tech. Note (February 4, 1966).

4. Cataldo, C. E., Effect of Hydrogen on Metals, NASA Tech. Brief 69-10372 (September 1969).

Key words: Chemical reactions; environment effects; hydrides; low temperature; temperature effects.

RELATION BETWEEN HYDROGEN EMBRITTLEMENT AND THE FORMATION OF HYDRIDE IN GROUP V TRANSITION METALS

Owen, C. V. and Scott, T. E. (Ames Lab., Iowa; Iowa State Univ. of Science and Technology, Ames)

Met. Trans. 3, 1715-1726 (July 1972).

The embrittlement of vanadium and tantalum by hydrogen has been investigated with the ultimate goal being to answer three specific questions concerning ductility behavior in different temperature ranges. Torsion pendulum internal friction and another technique using the torsion pendulum as well as visual observations have been used to establish the solid solubility curve in the V-H and Ta-H systems. The primary variables studied in this work were tensile strain rate, test temperature and hydrogen content. The results have been analyzed and tentative hypotheses have been set forth to explain ductility behavior of the hydrogen charged metals.

Important References:

1. Westlake, D. G., A Generalized Model for Hydrogen Embrittlement, Trans. ASM 62, No. 4, 1000-1006 (1969).

2. Westlake, D. G., A Resistometric Study of Phase Equilibria at Low Temperatures in the Vanaduim-Hydrogen System, Trans. AIME 239, 1341 (1967).

3. Sherman, D. H., Owen, C. V. and Scott, T. E., The Effect of Hydrogen on the Structure and Properties of Vanaduim, Trans. AIME 242, 1775 (1968).

Key words: Ductility; embrittlement; hydrides; hydrogen charging; metallic materials; temperature effects; tensile properties.

HYDROGEN EMBRITTLEMENT OF STAINLESS STEELS BY LITHIUM HYDRIDE
Thompson, A. W. (Sandia Labs., Livermore, CA)
Met. Trans. 5, 2819-2825 (December 1973).

Tests were made on 304L and 17-7 PH stainless steels in contact with LiH powder. Reduction in area relative to ductility in air decreased for both alloys. It was essential that the LiH be baked in contact with the alloys for the ductility loss to be observed; thermodynamic and kinetic evidence indicated that the LiH was reacting with surface oxides to furnish (H) to the steel. The depth to which hydrogen affected fracture morphology in 304L was greater than could be accounted for by diffusion, and it was concluded that dislocation transport accounted for the difference. Although direct evidence was not available, the locale of hydrogen damage in 304L was suggested to be the interface between the matrix and nonmetallic inclusions. A rationale based on this possibility was shown to be self-consistent. The generality of the importance of (H) furnished by LiH reaction was illustrated by the results on 17-7 PH.

Comment:

Two other significant papers are Thompson's "Ductility Losses in Austenitic Stainless Steels," (see below in Section III.C.4) and his "The Mechanism of Hydrogen Participation in Ductile Fracture," presented at the 1975 International Conference on the Effect of Hydrogen on the Behavior of Materials at Moran, WY.

This paper presented experimental evidence of hydrogen transport through the metal at a rate greater than could be accounted for by diffusion. The postulation of dislocation transport or pipes for the hydrogen has since received considerable theoretical and experimental effort. It is now accepted as a significant transport mechanism for the hydrogen in these alloys.

Important References:

1. Vennett, R. M. and Ansell, G. S., The Effect of High-Pressure Hydrogen Upon the Tensile Properties and Fracture Behavior of 304L Stainless Steel, Trans. ASM 60, 242-251 (1967).

2. Benson, Jr., R. B., Dann, R. K. and Roberts, Jr., L. W., Hydrogen Embrittlement of Stainless Steel, Trans. AIME 242, 2199-2205 (1968).

3. Louthan, Jr., M. R., Caskey, Jr., G. R., Donovan, J. A. and Rawl, Jr., D. E., Hydrogen Embrittlement of Metals, Mater. Sci. Eng. 10, 357-368 (1972)

Key words: Diffusion; dislocations (materials); ductility; fractures (materials); hydrogen embrittlement; stainless steels; tensile tests.

ROLE OF HYDROGEN IN STRESS CORROSION CRACKING OF AUSTENITIC STAINLESS STEELS
Mehta, M. L. and Burke, J. (University Coll. of Swansea, Wales)
Corrosion 31, No. 3, 108-110 (March 1975).

The tensile properties of Types 304L and 310 austenitic stainless steels have been studied at 20° and 150°C after cathodically charging with hydrogen at 100°C. The charging conditions were such as to avoid the complicating effects of hydrogen induced phase changes and surface cracking. It was found that a substantialdecrease in ductility and flow stress was produced by the dissolved hydrogen. This is an intrinsic effect and not a consequence of phase changes caused by the hydrogen. This experimental result will help to clarify the current controversy concerning the role of hydrogen in stress corrosion cracking by eliminating the necessity to involve hydrogen induced martensite.

Comment:

These experimental results which separate the hydrogen-induced martensite from stress corrosion in austenitic stainless steels should be helpful in furthering an understanding of these phenomena.

Important References:

1. Staehle, R. W., The Theory of Stress Corrosion Cracking in Alloys, J. E. Scully, Ed., NATO, Brussels (1971).

2. Theu, G. J. and Staehle, R. W., Proc. Int. Conf. Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys, Firminy, France (June 1973).

3. Burke, J., Mehta, M. L. and Narayan, R., Hydrogen in Metals, Proc. Int. Conf., Paris (1972).

Key words: Absorption; austenitic steels; diffusion; ductility; elongation; gas embrittlement; stainless steels; stress corrosion cracking; tensile properties.

THE ROLE OF HYDROGEN IN THE STRESS CORROSION CRACKING OF TITANIUM ALLOYS
Orman, S. and Picton, G. (Atomic Weapons Research Establishment, Aldermaston England)
Corros. Sci. 14, 451-459 (July 1974)

Work with Ti-8Al-1Mo-1V has shown that the susceptibility of this alloy to stress corrosion cracking (SCC) in dilute saline solution is dependent on the hydrogen content of the material. Progressive removal of hydrogen results in increasing K_{IC} and K_{ISCC} until at about the 5 ppm level the material shows immunity to SCC. Addition of hydrogen also raises the level of the fracture toughness values of the material when tested in air or saline, but does not confer immunity to SCC. Removal of hydrogen has a similar effect on the fracture toughness properties of Ti-6Al-4V.

Important References:

1. Seagle, S. R., Seeley, R. R. and Hall, G. S., Applications and Related Phenomena in Titanium Alloys, ASTM STP-432, 170-188 (1968).

2. Mukherjee, A. K., The Possible Role of Hydrogen in the Stress Corrosion Cracking of Titanium Alloys, Boeing Report No. D6-23621 (September 1967).

3. Howe, D. G. and Goode, R. J., Applications and Related Phenomena in Titanium Alloys, ASTM STP-432, 189-201 (1968).

4. Sandoz, G., Subcritical Crack Propagation in Ti-8Al-1Mo-1V Alloy in Organic Environments, Salt Water, and Inert Environments, Proc. Conf. Fundamental Aspects of SCC, Ohio State Univ., 684-690 (1969).

5. Feeney, J. A. and Blackburn, M. J., The Theory of SCC in Alloys, NATO Conf., Portugal (1971).

Key words: Experimentation; fracture strength; hydrogen embrittlement; stress corrosion cracking; stress intensity factor; test procedures; titanium alloys.

CATHODIC PROTECTION AND HYDROGEN IN STRESS CORROSION CRACKING
Barth, C. F. and Troiano, A. R. (TRW Equipment Labs., Cleveland, OH; Case Western Reserve Univ., Cleveland, OH)
Corrosion 28, No. 7, 259-263 (July 1972).

The relationship between brittle delayed failure under stress, hydrogen permeation, and applied potential has been examined for a high strength steel in an aerated and deaerated 3N NaCl environment. In the presence of oxygen at low cathodic potentials, no hydrogen permeation was detected and the brittle delayed failure characteristics were minimized, thus exhibiting the usual behavior associated with cathodic protection. However, in the absence of oxygen, substantial hydrogen permeation and brittle delayed failure were observed at precisely the same cathodic potentials as employed in the aerated solution. Thus, a definite one-to-one correlation exists between hydrogen availability for embrittlement and stress corrosion cracking (SCC). It is concluded that the phenomenon of cathodic protection does not rule out a hydrogen embrittlement mechanism for SCC. Under anodic potentials, the relation between hydrogen permeation with pitting and brittle delayed failure was confirmed.

Comment:

In this paper the authors have done a critical experiment in which they have shown that the cathodic potential argument against the role of hydrogen in SCC is not supported by the experimental facts. This was one of the key experiments helping to establish the role of hydrogen in SCC.

Important References:

1. Matsushima, I., Deegan, D., and Uhlig, H. H., Stress Corrosion and Hydrogen Cracking of 17-7 Stainless Steel, Corrosion 22, No. 1, 23-27 (1966).

2. Troiano, A. R. and Whiteman, M. B., Hydrogen Embrittlement of Austenitic Stainless Steel, Corrosion 21, No. 2, 53-56 (1965).

3. Shively, J. H., Hehemann, R. F., and Troiano, A. R., Hydrogen Permeability in Stable Austenitic Stainless Steel, Corrosion 22, No. 9, 253-256 (1966).

4. Shively, J. H., Hehemann, R. F., and Troiano, A. R., Hydrogen Permeability of a Stable Austenitic Steel under Anodic Polarization, Corrosion 23, No. 7, 215-217 (1967).

5. Barth, C. F., Steigerwald, E. A., and Troiano, A. R., Hydrogen Permeability and Delayed Failure in Polarized Martensitic Steels, Corrosion 25, No. 9, 353-358 (1969).

Key words: Cathodic protection; corrosion; delayed failure; embrittlement; hydrogen charging; pitting corrosion; stress corrosion cracking.

STRESS-CORROSION CRACKING AND HYDROGEN-STRESS CRACKING OF HIGH STRENGTH STEEL
Fletcher, E. E., Berry, W. A., and Elsea, A. R. (Battelle Memorial Institute, Columbus, OH)
DMIC Report 232 (July 1966).

Two fracture mechanisms are considered: stress corrosion cracking and hydrogen stress cracking. The purpose of the report is to identify where the two mechanisms are similar and how they differ. The important factors that influence the tendency to promote cracking by the two mechanisms are reviewed in detail. These factors are strength level, steel composition, steel structure, applied and residual stresses, environment (whereby there is a tendency toward corrosion or the introduction of hydrogen into steel), and time.

Important References:

1. Swann, P. R., Stress Corrosion Failure, Sci. Amer. 214, No. 2, 72-81 (February 1966).

2. Gray, H. R. and Troiano, A. R., How Hydrogen Affects Maraging Steel, Metal Progr. 85, No. 4, 75-78 (April 1964).

3. Groeneveld, T. P., Fletcher, E. E., and Elsea, A. R., A Study of Hydrogen Embrittlement of Various Alloys, NASA CR-77374 (June 1966).

4. Matsushima, I., Deegan, D., and Uhlig, H. H., Stress Corrosion and Hydrogen Corrosion Cracking of 17-7 Stainless Steel, Corrosion 22, No. 1, 23-27 (January 1966).

5. Dean, S. W. and Copson, H. R., Stress Corrosion Behavior of Maraging Nickel Steels in Natural Environments, Corrosion 21, No. 3, 95-103 (March 1965).

6. Tiner, N. A., Gilpin, C. B., and Toy, S. M., A Microstructural Study of Stress Corrosion Cracking in Martensitic 4340 Steel, Douglas Aircraft Co. Paper No. 3381 (June 1965).

Key words: Brittle fractures; corrosion; cracking (fracturing); failures (materials); fractures (materials); high strength steels; hydrogen embrittlement; material degradation; stress corrosion cracking.

CATALYTIC DISSOCIATION, HYDROGEN EMBRITTLEMENT, AND STRESS CORROSION
Liu, H. W. and Ficalora, P. J. (Syracuse Univ., NY)
Int. J. Fract. Mech. 8, 223-226 (June 1972).

In this technical note an experiment is described to prove the proposition that catalytic dissociation is the first step of the complicated processes that lead to hydrogen embrittlement and stress corrosion cracking. Fatigue-cracked 4340 steel specimens were used. Three experiments are described where specimens are subjected to constant loads in pure hydrogen and hydrogen/sulfur dioxide environments. Experimental data is reported and compared to other work reported in the literature.

Comment:

The authors report a critical experiment in which by the use of kinetic reactant poisons they examine the postulation that the first step in the hydrogen embrittlement, SCC mechanism is a catalytic dissociation of the hydrogen molecule. They show conclusively that for the ultra high strength 4340 steel employed in the experiment it is necessary for catalytic dissociation of the hydrogen molecule to occur in order for subsequent hydrogen embrittlement and stress corrosion cracking to proceed. Further work is necessary to determine if this catalytic dissociation is rate controlling.

Important References:

1. Fontana, M. G., 1970 Campbell Memorial Lecture, Met. Trans. 1, 3251 (1970).

2. Johnson, H. H. and Paris, P. C., Subcritical Flaw Growth, Eng. Fract. Mech. 1, 3-45 (June 1968).

3. Tetelman, A. S., The Hydrogen Embrittlement of Ferrous Alloys, in Fracture of Solids, 671-708 (1962).

4. Barth, C. F. and Steigerwald, E. A., Evaluation of Hydrogen Embrittlement Mechanics, Met. Trans. 1, 3451-3455 (December 1970).

Key words: Adsorption; cracking (fracturing); dislocations (materials); embrittlement; experimental data; failures (materials); gas embrittlement; hydrogen; stress corrosion cracking; test specimen design.

THE INFLUENCE OF LOADING MODE ON THE STRESS CORROSION SUSCEPTIBILITY OF VARIOUS ALLOY ENVIRONMENT SYSTEMS

Green, J. A. S., Hayden, H. W., and Montague, W. G. (Martin Marietta Labs., Baltimore MD)

Martin Marietta Corp. Report MML-TR-75-30C (1975).

The influence of loading mode on stress corrosion susceptibility has been examined for the following systems: Ti-8Al-1Mo-1V alloy/aqueous chlorides; alpha-brass/ammoniacal environments; 7076-T6 alloy in $NaCl/K_2Cr_2O_7$ solutions. With the exception of the alpha-brass/ammonia system, the stress corrosion susceptibility of the metal was found to be much greater under tensile (Mode 1) loading than torsional (Mode III) loading. Further, in certain instances the addition of hydrogen-recombination (cathodic) poisons, i.e., arsenic, was found to enhance susceptibility under tensile, but not torsional loading. This difference in susceptibility to cracking as a function of loading mode is interpreted to indicate that hydrogen damage is the dominant mechanism leading to failure. Implications of these results to mechanistic understanding are discussed.

Comment:

This report contains some additional experimental information and discussion of the experiments reported in earlier publications. The authors have performed a critical experiment which for the systems studied conclusively demonstrates the requirement for triaxial tensile stress in the crack tip region to provide a driving force for the hydrogen transport.

Important References:

1. Green, J. A. S. and Hayden, H. W., Influence of Two Modes of Loading on the Stress Corrosion Susceptibility of Ti-8Al-1Mo-1V Alloy in Various Chloride-Containing Environments, in Hydrogen in Metals, ASM, 235-249 (1974).

2. St. John, C. and Gerberich, W. W., The Effect of Loading Mode on Hydrogen Embrittlement, Met. Trans. 4, 589-594 (February 1973).

Key words: Aluminum alloys; cracking (fracturing); damage; embrittlement; environment effects; failure mechanisms; hydrogen; loads (forces); material degradation; stress corrosion; titanium alloys.

IIE - Crack Growth/Fracture Mechanics

FRACTURE MECHANICS CONSIDERATION OF HYDROGEN SULFIDE CRACKING IN HIGH STRENGTH STEELS
Bucci, R. J., Paris, P. C., Loushin, L. L., and Johnson, H. H., (Del Research Corp., Bethelehem, PA, Esso Research and Engineering Co., Linden, NJ, Cornell Univ, Ithaca, NY)
Stress Analysis and Growth of Crack, ASTM STP-513, 292-307 (September 1972).

Hydrogen sulfide (H_2S) stress corrosion cracking studies were conducted within the framework of fracture mechanics for several high strength steels (AISI 4340, 4140, HY-80, and HY-130). For all the steels and strength levels investigated (σ_{ys} = 80 to 150 ksi), H_2S stress corrosion cracking was found to exist. For each of the alloys investigated, a valid plane strain K_{ISCC} (which indicates the demarcation between detectable rates of crack extension, $\Delta a/\Delta t \geq 10^{-5}$ in/min and those below these rates) was measured and found to depend significantly on yield stress with decreasing K_{ISCC} values reported for increasing yield stress.

A limited investigation of crack growth kinetics found crack growth rates to accelerate most rapidly from presharpened fatigue cracks when loaded to K levels just beyond the K_{ISCC} threshold. In several instances, especially with the highest strength alloys, stress corrosion crack velocities attained peak values before being "damped" to some steady state velocity at increased K levels. The crack velocity damping might in part be attributed to crack division or plasticity effects associated with increasing plastic zone size to thickness ratio at higher K levels.

Comment:

These fracture toughness measurements in the aggressive hydrogen sulfide environment illustrate the usefulness of the fracture mechanics approach. As with most determinations of K_{ISCC}, the accuracy of the value is related to the time of exposure; thus presenting problems in relating one alloy to another. Nevertheless, the trends and relationships observed are valid.

Important References:

1. Dvoracek, L. M., Sulfide Stress Corrosion Cracking of Steels, Corrosion 26, No. 5, 177-188 (May 1970).

2. Novak, S. R. and Rolfe, S. T., Comparison of Fracture Mechanics and Nominal Stress Analysis in Stress Corrosion Cracking, Corrosion 26, No. 4, 121-130 (April 1970).

3. Wessel, E. T., State of the Art of the WOL Specimen for K_{IC} Fracture Toughness Testing, Eng. Fract. Mech. 1, No. 1, 77-103 (June 1968).

4. Gallagher, J. P., Corrosion Fatigue Crack Growth Behavior Above and Below K_{ISCC}, NRL Report 7064 (May 28, 1970).

Key words: Crack initiation; fracture mechanics; fractures (materials); high strength alloys; hydrogen embrittlement; stress corrosion.

ON THE THEORY OF CRACK GROWTH DUE TO HYDROGEN EMBRITTLEMENT

Cherepanov, G. P. (Moscow Mining Inst., USSR)

Corrosion 29, No. 8, 305-309 (August 1973).

The mathematical model offered for description of subcritical crack growth due to local hydrogen embrittlement is based on the assumptions: (1) the crack tip is a source of atomic hydrogen in metal; (2) the rate of the source is directly proportional to the crack opening displacement, the proportionality coefficient being determined by a certain electrochemical reaction; and (3) the effect of atomic hydrogen on a metal is fully described by the magnitude of their local concentration. The combined analysis of two different processes is advanced. The first is the local diffusion of atomic hydrogen near a crack tip; the other is the elastic-plastic deformation of fine and superfine structure of the crack tip. In result, the theoretical dependence of crack growth velocity on stress intensity factor is obtained. It is approximated by the linear diagram in the range of practical interest. The analysis of some test data of Carter, Johnson, Ryder, and others is also given.

Important References:

1. Johnson, H. H. and Paris, P. C., Subcritical Flaw Growth, Eng. Fracture Mech. 1, No. 3 (1968).

2. Ryder, J. T. and Gallagher, J. P., Environmentally Controlled Fatigue Crack-Growth Rates in SAE 4340 Steel-Temperature Effects, Trans. ASME 92, 133 (1970).

3. Carter, C. S., Stress Corrosion Crack Branching in High Strength Steels, Eng. Fract. Mech. 3, No. 1 (1971).

Key words: Brittle fractures; crack propagation; corrosion; high strength steels; hydrogen embrittlement; maraging steels; mathematical models; stress corrosion cracking; stress intensity factor; subcritical crack growth.

THE STRESS INTENSITIES FOR SLOW CRACK GROWTH IN STEELS CONTAINING HYDROGEN

Dautovich, D. P. and Floreen, S. (International Nickel Co., Inc., NY)

Met. Trans. 4, 2627-2630 (November 1973).

A test technique has been developed to determine the stress intensity for slow crack growth in hydrogen precharged steels. Measurements on several grades of maraging steel and a 300M steel show that hydrogen contents on the order of 2 ppm reduce the stress intensity for slow crack growth by 50 percent or more of the K_{IC} values. At equivalent hydrogen contents the 300M steel was more severely embrittled than the maraging steels. Comparison of the present results with aqueous K_{ISCC} data indicates that the amount of hydrogen picked up by the steels in stress corrosion increases with increasing yield strength.

Comment:

The authors have identified that relationships exist between stress intensity, slow crack growth, yield strength and hydrogen. These appear to be significant, however, more experimental effort will be required before the full role of hydrogen in this area can be illuminated.

Important References:

1. Smith, J. A., Peterson, M. H. and Brown, B. F., Electrochemical Conditions at the Tip of an Advancing Stress Corrosion Crack in AISI 4340 Steel, Corrosion 20, 539 (1970).

2. Sandoz, G., A Unified Theory for Some Effects of Hydrogen Source, Alloying Elements, and Potential on Crack Growth in Martensitic AISI 4340 Steel, Met. Trans. 3, 1169-1176 (May 1972).

3. Beachem, C. D., A New Model for Hydrogen Assisted Cracking (Hydrogen Embrittlement), Met. Trans. 3, No. 2, 437-451 (February 1972).

4. Sandoz, G., Effects of Alloying Elements on the Susceptibility to Stress Corrosion Cracking of Martensitic Steels in Salt Water, Met. Trans. 2, No. 4, 1055-1063 (April 1971).

5. Brown, B. F., The Application of Fracture Mechanics to Stress Corrosion Cracking, Metals Mater. 2, No. 12, 171-183 (1968).

Key words: High strength alloys; hydrogen embrittlement; stress corrosion; stress intensity factor; subcritical crack growth.

EFFECT OF HYDROGEN ON FRACTURE AND INERT-ENVIRONMENT SUSTAINED LOAD CRACKING RESISTANCE OF ALPHA-BETA TITANIUM ALLOYS

Meyn, D. A. (Naval Research Lab., Washington, DC)

Met. Trans. 5, 2405-2414 (November 1974).

The fracture toughness and resistance to inert-environment sustained load crack propagation of alpha-beta titanium alloys are usually reduced by increased hydrogen content. The range of hydrogen content over which fracture toughness or threshold stress intensity for sustained load cracking was observed to decrease when hydrogen content is small (0 to 50 ppm) for Ti-6Al-4V, but further increases in hydrogen content can cause an increase in cracking rates. Sustained load crack propagation is characterized by a mixture of microvoid coalescence with cleavage, usually on a plane 12 to 15 degrees from 0001 of the HCP alpha phase with some 0001 cleavage. Cleavage apparently initiates ahead of the main crack front within alpha grains, usually near apparent alpha-beta interfaces. Atmospheric moisture is inert with respect to sustained load cracking, that is, it does not cause stress corrosion cracking. Sustained load cracking was demonstrated in Ti-8Al-1V, Ti-6Al-6V-2Sn, and several grades of Ti-6Al-4V.

Important References:

1. Sandoz, G., Subcritical Crack Propagation in Ti-8Al-1Mo-1V Alloy in Organic Environments, Salt Water, and Inert Environments, Proc. Conf. Fundamental Aspects of Stress Corrosion Cracking, NACE, Houston, TX (1969).

2. Williams, D. N., Subcritical Crack Growth in Two Titanium Alloys, Met. Trans. 4, 675-680 (1973).

3. Meyn, D. A., Cleavage in Ti-8Al-1Mo-1V Caused by Hydrogen Gas, Met. Trans. 3, 2302-2305 (1972).

4. Wei, R. P. and Ritter, D. L., The Influence of Temperature on Fatigue Crack Growth in a Mill Annealed Ti-6Al-4V Alloy, J. Mater. 7, No. 2, 240-250 (1972).

5. Wanhill, R. J. H., A Consideration of Cleavage in Alpha Titanium, Acta Met. 21, 1253-1258 (1973).

6. Beachem, C. D., A New Model for Hydrogen Assisted Cracking (Hydrogen Embrittlement), Met. Trans. 3, 437-451 (1972).

Key words: Crack propagation; environment effects; fracture analysis; fractures (materials); hydrogen environment embrittlement; microstructure; static crack growth; stress corrosion cracking; stress intensity factor; titanium alloys.

QUANTITATIVE OBSERVATIONS OF HYDROGEN-INDUCED, SLOW CRACK GROWTH IN A LOW ALLOY STEEL

Nelson, H. G. and Williams, D. P. (National Aeronautics and Space Administration, Ames Research Center, Moffett Field, CA)

NASA TM-X-62253 (March 1973).

Environmental hydrogen embrittlement of iron-base alloys is a complex phenomenon and is shown in this study to remain complex even under systematic investigation in simple, well-characterized environments using a single alloy system and a single test technique. Hydrogen-induced slow crack growth was studied in 4130 low alloy steel in gaseous hydrogen and distilled water environments as a function of applied stress intensity at various temperatures, hydrogen pressures, and alloy strength levels. The results of this study provide support for most of the qualitative predictions of the lattice decohesion theory as modified by Oriani.

Comment:

The importance of this paper is the demonstration that even with significant experimental simplification it was not possible to significantly decrease the complexity of the hydrogen-induced slow crack phenomena.

Important References:

1. Sawicki, V. R., Hydrogen Induced Cracking in a High Strength Steel, PhD Dissertation, Cornell Univ., NY (1971).

2. Hydak, Jr., S. J., The Kinetics of Hydrogen Enhanced Crack Growth in High Strength Steels, MS Thesis, Lehigh Univ., PA (1972).

3. Nelson, H. G., The Kinetic and Mechanical Aspects of Hydrogen-Induced Failure in Metals, NASA TN-D-6691 (1972).

4. Van der Sluys, W. A., Mechanisms of Environment Induced Subcritical Crack Growth in AISI 4340 Steel, T&AM Report 292, Illinois Univ., IL (1966).

Key words: Crack propagation; embrittlement; environment effects; fractures (materials); hydrogen environment embrittlement; stress intensity factor.

EQUILIBRIUM ASPECTS OF HYDROGEN-INDUCED CRACKING OF STEELS
Oriani, R. A. and Josephic, P. H. (United States Steel Corp., Monroeville, PA)
Acta Met. 22, 1065-1074 (September 1974).

The threshold pressures of hydrogen and of deuterium gases necessary to cause crack propagation in AISI 4340 of 250 psi yield strength have been determined as a function of plane strain stress intensity factor at room temperature. The functional threshold pressure is shown to be well fitted by an analytical expression derived from the unstable equilibrium form of the decohesion theory plus some reasonable ad hoc assumptions for the necessary functional relationships. From the fitting of the theoretical equation to the experimental data numerical values are obtained for the hydrostatic component of the stress at the crack front, for the equilibrium enhancement of concentration of hydrogen, and for the reduction by the hydrogen of the maximum cohesive resistive force. The magnitudes of these numbers and their trends with plane strain stress intensity factor are in agreement with expectations from the decohesion theory but with no other extant point of view.

Comment:

This experimental demonstration is shown to support the basic postulates of Oriani's decohesion theory published in 1972 and 1973. During cracking there are two mechanisms in operation: (1) the decohesion at grain and interphase boundaries, and (2) plastic tearing. Only the former appears to be aided by hydrogen and is characteristic of hydrogen-induced cracking.

Important References:

1. Oriani, R. A., Proc. Int. Conf. Stress Corrosion Cracking and Hydrogen Embrittlement of Iron-Base Alloys, Firminy, France (June 1973).

2. Williams, D.P. and Nelson, H. G., Embrittlement of 4130 Steel by Low-Pressure Gaseous Hydrogen, Met. Trans. 1, 63-68 (1970).

3. Rath, B. B. and Bernstein, I. M., The Relation Between Grain-Boundary Orientation and Intergranular Cracking, Met. Trans. 2, 2845-2851 (October 1971).

Key words: Crack propagation; cracking (fracturing); decohesion; gas embrittlement; high strength steels; hydrogen embrittlement; stress intensity factor.

GASEOUS HYDROGEN-INDUCED CRACKING OF Ti-5Al-2.5Sn

Williams, D. P. and Nelson, H. G. (National Aeronautics and Space Administration, Ames Research Center, Moffett Field, CA)

Met. Trans. 3, 2107-2113 (August 1972).

The kinetics of hydrogen-induced cracking were studied in Ti-5Al-2.5Sn alloy having acicular alpha platelets in a beta matrix structure. It was observed that the relationship between hydrogen-induced crack growth rate and applied stress intensity can be described by three separable regions of behavior. The crack growth rate at low stress intensity levels was found to be exponentially dependent on stress intensity but essentially independent of temperature. The crack growth rate at intermediate stress intensity levels was found to be independent of stress intensity but dependent on temperature. The crack growth rate at stress intensity levels very near the fracture toughness is presumed to be independent of environments.

Important References:

1. Nelson, H. G., Williams, D. P. and Stein, J. E., Environmental Hydrogen Embrittlement of an Alpha-Beta Titanium Alloy Effect of Microstructure, Met. Trans. 3, 469-475 (1972).

2. Nelson, H. G., Environmental Hydrogen Embrittlement of Titanium - A Qualitative Comparison with Stress Corrosion Cracking, Proc. Int. Conf. Stress Corrosion Cracking Mechanisms in Titanium Alloys, Atlanta, GA (1971).

3. Bixler, W. D., Flaw Growth of Inconel 718 and 5 Al - 2.5Sn (ELI) Titanium in a High Purity Gaseous Hydrogen Environment, Aerojet Nuclear Systems Co., CA (August 1971).

Key words: Cracking (fracturing); embrittlement; hydrogen; material degradation; stress intensity factor; titanium alloys.

III - HYDROGEN EFFECTS ON MATERIAL SYSTEMS

STRESS-CORROSION AND HYDROGEN-EMBRITTLEMENT BEHAVIOR OF LINE-PIPE STEEL IN UNDERGROUND ENVIRONMENTS
Vrable, J. B. (West Virginia, Univ., Morgantown, WV)
W. Va. Univ., Eng. Exp. Sta., Tech. Bull. No. 106, 299-310 (1972).

Over the years, stress corrosion cracking has been encountered in carbon steels and low-alloy steels in only a very limited number of corrosive environments. The most common of these are hot and concentrated nitrate environments, hot caustic solutions, contaminated anhydrous ammonia, and, for higher strength steels, sulfide environments. In the recent past, however, there have been several failures of gas-transmission pipelines that have been attributed to stress-corrosion cracking under soil exposure conditions which do not correspond with any of the previous environments known to cause these phenomena. Moreover, cracking-type failures initiating in "hard spots" have been attributed to hydrogen embrittlement. As a result of these reports, a substantial interest has developed in establishing valid methods for detecting and recognizing stress-corrosion cracking and hydrogen embrittlement in line-pipe steels. The characteristics of both of these types of cracking are described. In addition, several examples of pipeline cracking are cited with emphasis on the investigative work performed to establish the cause and the nature of these cracks. Current thinking with respect to avoiding stress corrosion and hydrogen embrittlement in future installations is also described.

Comment:

The author's observation of the relationship between field failures and hard spots in the steel is very significant. Two consequences of this observation have resulted. First, a very detailed set of materials specifications has been developed. These are focused on the procurement of pipeline steel without hard spots. Second, the observation has focused the theoretical efforts on understanding the nature of these hard spots and how they become fracture locations.

Important References:

1. Treseder, R. S. and Swanson, T. M., Factors in Sulfide Corrosion Cracking of High Strength Steels, Corrosion 24, 31 (1968).

2. Elsea, A. R. and Fletcher, E. E., Hydrogen-Induced, Delayed, Brittle Failures of High-Strength Steels, DMIC Report 196 (January 1964).

3. Oriani, R. A., Hydrogen in Metals, Proc. NACE Symp. on Fundamental Aspects of Stress-Corrosion Cracking (1969).

Key Words: Brittle fractures; carbon steels; corrosion; environmental effects; failures (materials); hydrogen embrittlement; pipes (tubes); steels.

FRACTURE MECHANICS CONSIDERATION OF HYDROGEN SULFIDE CRACKING IN HIGH STRENGTH STEELS

Bucci, R. J., Paris, P. C., Loushin, L. L., and Johnson, H. H., (Del Research Corp., Bethlehem, PA, Esso Reserach and Engineering Co., Linden, NJ, Cornell Univ., Ithaca, NY)

Stress Analysis and Growth of Crack, ASTM STP-513, 292-307 (September 1972).

Hydrogen sulfide (H_2S) stress corrosion cracking studies were conducted within the framework of fracture mechanics for several high strength steels (AISI 4340, 4140, HY-80 and HY-130). For all the steels and strength levels investigated (σ_{ys} = 80 to 150 ksi), H_2S stress corrosion cracking was found to exist. For each of the alloys investigated, a valid plane strain K_{ISCC} (which indicates the demarcation between detectable rates of crack extension, $\Delta a/\Delta t \geq 10^{-5}$ in/min and those below these rates) was measured and found to depend significantly on yield stress with decreasing K_{ISCC} values reported for increasing yield stress.

A limited investigation of crack growth kinetics found crack growth rates to accelerate most rapidly from presharpened fatigue cracks when loaded to K levels just beyond the K_{ISCC} threshold. In several instances, especially with the highest strength alloys, stress corrosion crack velocities attained peak values before being "damped" to some steady state velocity at increased K levels. The crack velocity damping might in part be attributed to crack division or plasticity effects associated with increasing plastic zone size to thickness ratio at higher K levels.

(FOR LISTING OF IMPORTANT REFERENCES, KEYWORDS AND A DUPLICATE ABSTRACT, SEE PAGE 50).

STRESS-CORROSION CRACKING AND HYDROGEN-STRESS CRACKING OF HIGH STRENGTH STEEL

Fletcher, E. E., Berry, W. A., and Elsea, A. R. (Battelle Memorial Institute, Columbus, OH)

DMIC Report 232 (July 1966).

Two fracture mechanisms are considered: stress corrosion cracking and hydrogen stress cracking. The purpose of the report is to identify where the two mechanisms are similar and how they differ. The important factors that influence the tendency to promote cracking by the two mechanisms are reviewed in detail. These factors are strength level, steel composition, steel structure, applied and residual stresses, environment (whereby there is a tendency toward corrosion or the introduction of hydrogen into steel), and time.

(FOR LISTING OF IMPORTANT REFERENCES, KEYWORDS AND A DUPLICATE ABSTRACT, SEE PAGE 47).

FACTORS AFFECTING THE SULFIDE STRESS CRACKING PERFORMANCE OF HIGH STRENGTH STEELS
Greer, J. B. (Esso Production Co., Houston, TX)
Mater. Perfor., 11-22 (March 1975).

Environmental, metallurgical, and stress effects on high strength steel performance in sour environments are summarized. Environmental variables with respect to manufacture and design of tubular goods for deep, sour wells are interpreted. A large number of illustrations are used to present time-to-failure data, hydrogen penetration rate as a function of H_2S concentration, temperature effects, fatigue curves, etc. There are 51 references.

Comment:

The author has presented a wealth of empirical information on the sulfide stress cracking problem. It is of interest to note that the high strength steels considered in this paper are in the 125 to 150 thousand psi range. This paper highlights the empirical approach that the industry has been forced to employ in attacking this problem. This illustrates the necessity for theoretical work in this area and the transfer of this to the practical sphere.

Important References:

1. Phelps, F. H., A Review of the Stress Corrosion Behavior of Steels with High Yield Strength, Proc. Conf. Fundamental Aspects of Stress Corrosion Cracking, NACE (1969).

2. Hudgins, C. M., The Effect of Temperature on the Aqueous Sulfide Stress Cracking Behavior of an N-80 Steel, NACE Canadian Western Regional Conf. (1971).

3. Lasater, R. M., Kenney, B. R. and Knox, J. A., Prevention of Hydrogen Sulfide Cracking of High Strength Carbon Steels in Acid Systems, NACE 23rd Annu. Conf., (1967).

4. Judy, Jr., R. W. and Goode, R. J., Procedure for Stress Corrosion Cracking Characterization and Interpretation to Failure-Safe Design for High Strength Steels, Proc. NACE 26th Annu. Conf., (1970).

5. Novak, S. R. and Rolfe, S. T., Comparison of Fracture Mechanics and Nominal-Stress Analysis in Stress Corrosion Testing (Proc. 26th Annual Conf. NACE (1970)).

6. Bucci, R. J., Paris, P. C., Loushin, L. L. and Johnson, H. H., A Fracture Mechanics Consideration of Hydrogen Sulfide Cracking in High Strength Steels, ASTM STP-513, Part 1, 292-307 (September 1972).

Key words: Brittle fractures; corrosion; environmental effects; high strength steels; microstructures; stress corrosion cracking; sulfide stress cracking; temperature effects.

EQUILIBRIUM ASPECTS OF HYDROGEN-INDUCED CRACKING OF STEELS
Oriani, R. A. and Josephic, P. H. (United States Steel Corp., Monroeville, PA)
Acta Met. 22, 1065-1074 (September 1974).

The threshold pressures of hydrogen and of deuterium gases necessary to cause crack propagation in AISI 4340 of 250 psi yield strength have been determined as a function of plane strain stress intensity factor at room temperature. The functional threshold pressure is shown to be well fitted by an analytical expression derived from the unstable equilibrium form of the decohesion theory plus some reasonable ad hoc assumptions for the necessary functional relationships. From the fitting of the theoretical equation to the experimental data numerical values are obtained for the hydrostatic component of the stress at the crack front, for the equilibrium enhancement of concentration of hydrogen, and for the reduction by the hydrogen of the maximum cohesive resistive force. The magnitudes of these numbers and their trends with plane strain stress intensity factor are in agreement with expectations from the decohesion theory but with no other extant point of view.

(FOR LISTING OF IMPORTANT REFERENCES, KEYWORDS AND A DUPLICATE ABSTRACT, SEE PAGE 55).

EMBRITTLEMENT OF 4130 STEEL BY LOW-PRESSURE GASEOUS HYDROGEN
Williams, D. P. and Nelson, H. G. (National Aeronautics and Space Administration, Ames Research Center, Moffett Field, CA)
Met. Trans. 1, 63-68 (January 1970).

A study has been made of fully hardened 4130 steel in low-pressure, <760 torr, gaseous hydrogen. It was found that the embrittlement was caused by hydrogen-induced, slow crack growth. In the range of temperature from 80°C to 25°C, the crack growth rate increased with decrease in temperature; in the range from 0°C to -80°C, the rate decreased with decrease in temperature. It was also found that the crack growth rate had a different pressure dependence at high temperatures than at low temperatures. From a consideration of these experimental data, as well as from data from earlier investigations, it was determined that gaseous hydrogen embrittlement and the embrittlement of hydrogen-charged steels are basically the same phenomenon. The data are discussed in terms of a surface reaction model that adequately explains both gaseous hydrogen embrittlement and the embrittlement of hydrogen charged steels.

(FOR LISTING OF IMPORTANT REFERENCES, KEYWORDS AND A DUPLICATE ABSTRACT, SEE PAGE 31).

THE EFFECTS OF HIGH-PRESSURE HIGH-TEMPERATURE HYDROGEN ON STEEL
Fletcher, E. E. and Elsea, A. R. (Battelle Memorial Inst., Columbus, OH)
DMIC Report 202 (March 26, 1964).

This Battelle report describes the deleterious effects of hydrogen gas on steel at elevated temperatures and/or pressures. Factors that determine the degree of attack are temperature, hydrogen partial pressure, stress, exposure time, composition of the steel, and structure of the steel. For a given exposure time, hydrogen attack on steel starts at a limiting temperature and pressure. Longer exposure times permit attack to start at lower temperatures. Also, the higher the temperature, the lower the limiting pressure and vice versa. Prior cold work or creep during exposure accelerates the attack.

(FOR LISTING OF IMPORTANT REFERENCES, KEYWORDS AND A DUPLICATE ABSTRACT, SEE PAGE 36).

HYDROGEN MOVEMENT IN STEEL - ENTRY, DIFFUSION, AND ELIMINATION
Fletcher, E. E. and Elsea, A. R. (Battelle Memorial Inst., Columbus, OH)
DMIC Report 219 (June 1965).

This report was prepared to aid in understanding the movement of hydrogen in steel. It considers ways in which hydrogen enters steels, how it moves through steel, and methods whereby it may be removed from steel. The various factors that affect each of these phenomena are considered. The first section of the report deals with the solubility of hydrogen, and such aspects of solubility as preferred lattice sites for hydrogen, lattice expansion, measurements of solubility, and estimates of equilibrium hydrogen pressure in steel are discussed. The second section concerns the permeation of hydrogen through steel. Factors which influence the rate of hydrogen removal from iron and steel, such as temperature, section size, external environment, and coatings on the steel, are dealt with in the final section of the report.

Important References:

1. Cotterill, P., The Hydrogen Embrittlement of Metals, Progress in Metal Physics 9, 201-301, Pergamon Press, NY (1961).

2. Tetelman, A. S., Wagner, C. N. J., and Robertson, W. D., An X Ray Investigation of the Effects of Hydrogen in Iron, Acta Met. 9, 205-215 (1961).

3. Smialowski, M., Hydrogen in Steel, Pegamon Press (Oxford) (1962).

4. Hudson, R. M., Riedy, K. J., and Stragand, G. L., Influence of Cold-Reduction and Heat Treatment Combinations on Hydrogen Solubility and Permeability in Steel, Corrosion 17, No. 7, 334T-336T (1961).

5. Barton, R. J., The Mechanism of Transport of Hydrogen Across A Solution - Metal Interface, Hydrogen Embrittlement in Metal Finishing, Reinhold Pub. Co., NY, 20-45 (1961).

6. McNabb, A. and Foster, P. K., A New Analysis of the Diffusion of Hydrogen in Iron and Ferritic Steels, Trans. AIME 227, 618-627 (1963).

Key words: Coatings; corrosion; diffusion; environment effects; hydrogen; metallic materials; microstructures; solubility.

IIIB - Ultrahigh Strength Steels

EXPLORATORY DEVELOPMENT ON HYDROGEN EMBRITTLEMENT OF HIGH STRENGTH STEEL DURING MACHINING
Das, K. B. (Boeing Co., Seattle, WA).
AFML-TR-73-244 (1973).

The possibility of machining fluid being a source of hydrogen during the fabrication process was investigated. Failure of high strength steel structures can occur as a result of hydrogen embrittlement due to absorption during fabrication or when the hardware is in use. Test specimens made of 4340 steel (heat treated to 260 psi - 280 psi strength level) of known hydrogen concentration were subjected to a specified schedule of gentle and abusive milling and grinding operations using different machining fluids. Following the machining operations the specimens were analyzed for excess hydrogen above the base level with a Boeing-developed ultrasensitive hydrogen analysis system. A total of six different machining fluids with different active chemical components were used. Experimental results are presented with a statistical analysis of the hydrogen concentration data.

Important References:

1. Beck, W., Jankowsky, E. J., and Fischer, P., Hydrogen Stress Cracking of High Strength Steels, NADC-MA-7140 (1971).

2. Klier, E. P., Muvdi, B. E., and Sachs, G., The Response of High Strength Steels in the Range of 180 to 300 Ksi to Hydrogen Embrittlement from Cadmium Plating, Proc ASTM 58, 605 (1958).

Key words: Contamination; embrittlement; fabrication; high strength steels; hydrogen; machining; structural alloys.

ENVIRONMENTAL CRACK GROWTH BEHAVIOR OF HIGH STRENGTH PRESSURE VESSEL ALLOYS
Forman, R. G. (National Aeronautics and Space Administration, Lyndon B. Johnson Space Center, Houston, TX)
NASA TN-D-7952 (April 1975).

Results of sustained-load environmental crack growth threshold tests performed on six spacecraft pressure vessel alloys are presented. The alloys were Inconel 718, 6 Al - 4V Titanium, A-286 Steel, AM-350 Stainless Steel, Cryoformed AISI 301 Stainless Steel, and Cryoformed AISI 304L Stainless Steel. The test environments for the program were air; pressurized gases of hydrogen, oxygen, nitrogen, and carbon dioxide; and liquid environments of distilled water, sea water, nitrogen tetroxide, hydrazine, aerozine 50, monomethyl hydrazine, and hydrogen peroxide. The only severe environmental crack-growth problem found in the materials tested was in cryoformed 301 stainless steel exposed to gaseous hydrogen and aerozine and in Inconel 718 exposed to gaseous hydrogen. The A-286 steel had no incompatibility with high pressure gaseous hydrogen.

Important References:

1. Tiffany, C. F., Fracture Control of Metallic Pressure Vessels, NASA SP-8040 (1970).

2. Pettit, D. E., Fedderson, C. E., and Mindlin, H., Flaw Growth Behavior of Inconel 718 at Room and Cryogenic Temperature, NASA CR-101942 (1969).

Key words: Crack initiation; crack propagation; design criteria; fracture mechanics; pressure vessels; stress intensity factor.

EFFECT OF HYDROGEN ON HIGH STRENGTH AND MARTENSITIC STEELS
Gerberich, W. W. (Minnesota, Univ., Minneapolis)
Proc. Int. Conf. Effects of Hydrogen on Material Properties and Selection and Structural Design, Champion, PA
(23-27 September 1973).

The equilibrium and kinetic models for threshold and crack growth conditions were found to be consistent with available data on high strength steels. It was shown that it is reasonably certain that: (1) thresholds can be predicted based upon yield strength, concentration level and stress field variables, - increasing these variables decreases the threshold; (2) thresholds can be predicted under relatively plane stress and plane strain conditions - increasing plate thickness decreases the threshold; (3) Stage I, II and III crack growth rate observations can be explained on the basis of the hydrogen stress field interaction and the type of microscopic growth process; (4) extremes of plane stress and plane strain growth kinetics are due to large differences in the pressure tensor gradient. It has been hypothesized but with less certainty that: (1) the effect of alloying elements on the threshold are generally small - secondary effects are due to their influence on yield strength or initial hydrogen concentration levels; (2) the effect of tempering temperatures on threshold is only a yield strength effect - increased tempering temperatures produce higher thresholds; (3) the main effect of environment is to control the availability of atomic hydrogen at the crack tip; (4) tempering, aging and alloying parameters affect crack growth rate by controlling hydrogen trapping and yield strength. Alloy additions, which provide trap sites, may decrease kinetics by three orders of magnitude. Careful kinetic analyses of different alloying systems under varying experimental conditions must precede development of more accurate theoretical models.

(FOR LISTING OF IMPORTANT REFERENCES, KEYWORDS AND A DUPLICATE ABSTRACT, SEE PAGE 27).

EFFECT OF TEMPERATURE AND STATE OF STRESS ON HYDROGEN EMBRITTLEMENT OF HIGH STRENGTH STEEL
Greer, J. B., Von Rosenberg, E. L., and Martinez, J. (Esso Production Research Co., Houston, TX)
Corrosion 28, No. 19, 378-384 (1972).

Acidizing is a primary method of oil and gas well completion in carbonate formations and is frequently used as a stimulation technique in the shaley Gulf Coast sands. The question of the effect of acidizing on tubular goods has been of greater interest since the use of high strength materials in deep wells (acidizing depths have ranged to 22,000 feet). The two effects of acid on the steel are: (1) the corrosion and simple metal loss, and (2) embrittlement and catastrophic cracking of the material. Only the second of these is considered in this report.

(FOR LISTING OF IMPORTANT REFERENCES, KEYWORDS, AND A DUPLICATE ABSTRACT, SEE PAGE 37).

INFLUENCE OF PRELOADING ON THE SUSTAINED LOAD CRACKING BEHAVIOR OF MARAGING STEELS IN HYDROGEN
Jonas, O. (Westinghouse Electric Corp., Philadelphia, PA)
Corrosion 28, No. 8, 299-304 (August 1973)

Precracked center notch specimens of 18% Ni maraging steel (250) and (300) were preloaded in dry argon and air, respectively, to various percentages of K_{IC}, unloaded, and then threshold stress intensity K_{ISCC} was measured in dry hydrogen. A permanent, approximately linear increase of K_{ISCC} with K_I preload was observed. Fractography shows changes of a straight crack path in the location of a plastic zone developed due to crack preloading.

Important References:

1. Jonas, O. and Wei, R. P., An Exploratory Study of Delay in Fatigue Crack Growth, Int. J. Fract. Mech. 7, 116-118 (March 1971).

2. Carter, C. S., Effect of Prestressing on the Stress-Corrosion Resistance of Two High-Strength Steels, Met. Trans. 3, No. 2, 584-586 (February 1972).

3. Wei, R. P. and Landes, J. D., Correlation Between Sustained Load and Fatigue Crack Growth in High Strength Steels, Mater. Res. Stand. 9, No. 7, 25-28 (July 1969).

Key words: Cracks; fractures (materials); hydrogen; maraging steel; stress intensity factor; stress corrosion.

HYDROGEN EMBRITTLEMENT STUDIES OF A TRIP STEEL
McCoy, R. A. and Gerberich, W. W. (California Univ., Berkeley, Lawrence Berkeley Lab.)
Met. Trans. 4, 539-547 (February 1973)

The conditions of cathodic charging, gaseous hydrogen environment, and loading for which a TRIP steel may or may not be susceptible to hydrogen embrittlement were investigated. In the austenitic state, the TRIP steel appeared to be relatively immune to hydrogen embrittlement. It was shown that it is the strain-induced martensitic phase, α', which is embrittled. In TRIP steel single-edge-notch specimens under fixed loads in gaseous hydrogen, slow crack growth occurs when the stress intensity level exceeds a threshold level of about 25 ksi-in $^{1/2}$ and the growth rate varies approximately as the 2.5 power of the stress intensity level. The activation energy for this slow crack growth was found to be about 10,000 cal/g-atom, the approximate activation for hydrogen diffusion in martensite. Thus it was concluded that slow crack growth in TRIP steel loaded in gaseous hydrogen involves the diffusion of hydrogen through the α' phase.

Important References:

1. Elsea, A. R. and Fletcher, E. E., Hydrogen-Induced, Delayed, Brittle Failures of High Strength Steels, DMIC-196, Battelle Memorial Institute (January 1964).

2. McCoy, R. A., Gerberich, W. W., and Zackay, V. F., On the Resistance of TRIP Steel to Hydrogen Embrittlement, Met. Trans. 1, 2031-2034 (July 1970).

Key words: Crack initiation; crack propagation; hydrogen embrittlement; high strength steels; microstructure.

ON HYDROGEN BRITTLENESS IN HIGH STRENGTH STEELS
Johnson, H. H. (Cornell Univ., Ithaca, NY)
Fundamental Aspects of Stress Corrosion Cracking, R. A. Staehle, A. J. Forty, and D. Van Rooyen, Eds., NACE, 439-445 (1969).

Recent experiments on hydrogen and slow crack growth in high strength steels are discussed and interpreted in terms of current concepts of hydrogen brittleness. Crack growth activation energies for internal and external hydrogen environments are in agreement with the measured activation energy for hydrogen diffusion in a high strength steel.

Molecular hydrogen at atmospheric pressure induces a more severe brittleness than either water or the usual electrolytic charging conditions. It is concluded that the pressure mechanism of hydrogen embrittlement is not operative in high strength steels.

Comment:

Additional data, both experimental and theoretical, were reported by Johnson at the 1973 International Hydrogen Conference in Champion, PA (see Page 13).

Important References:

1. Van der Sluys, W. A., Mechanisms of Environment-Induced Subcritical Flaw Growth in AISI 4340 Steel, Paper at Natl. Symp. Fracture Mech., 1st, Lehigh Univ. (1967).

Key words: Brittleness; crack growth rate; crack propagation; deformation; diffusion; ductility; environment effects; experimental data; high strength steels; hydrogen.

A COMPARISON OF HYDROGEN EMBRITTLEMENT AND STRESS CORROSION CRACKING IN HIGH STRENGTH STEELS

Kortovich, C. S. and Steigerwald, E. A. (TRW Equipment Labs., Cleveland, OH)

Eng. Fract. Mech. 4, No. 4-D, 637-651 (1972).

The purpose of this study was to compare the known behavior of hydrogen embrittled high-strength steel to the characteristics of environmentally induced failure where hydrogen is continuously generated at the specimen surface. The incubation time for the initiation of slow crack growth was accelerated by prestressing for a fixed time below the lower critical limit. These results obtained on high-strength steel in a stress corrosion environment were directly comparable to behavior of hydrogenated specimens. These data along with hydrogen diffusivity measurements and the insensitivity of the incubation time and crack growth rate to specimen thickness indicated that the stress corrosion process was controlled by the distilled water-metal surface reaction.

Important References:

1. Barth, C. F. and Steigerwald, E. A., Evaluation of Hydrogen Embrittlement Mechanisms, Met. Trans. 1, 3451-3455 (December 1970).

2. Barth, C. F., Steigerwald, E. A., and Troiano, A. R., Hydrogen Permeability and Delayed Failure of Polarized Martensitic Steels, Corrosion 25, 353-358 (September 1969).

3. Brown, B. F., Fujii, C. T. and Dahlberg, E. P., Methods for Studying Solution Chemistry Within Stress Corrosion Cracks, J. Electrochem. Soc. 116, No. 2, 218-219 (February 1969).

4. Nanis, L. Contract NR 036-077 (1970).

5. Benjamin, W. D. and Steigerwald, E. A., Effect of Composition on the Environmentally Induced Delayed Failure of Precracked High-Strength Steel, Met. Trans. 2, 606-608 (1971).

Key words: Chemical reactions; crack growth rate; crack initiation; crack propagation; diffusion; embrittlement; environment effects; high strength steels; hydrogen embrittlement; material degradation; pre-cracked specimens; stress corrosion cracking.

IIIC - Stainless Steels

EFFECT OF HIGH DISLOCATION DENSITY ON STRESS CORROSION CRACKING AND HYDROGEN EMBRITTLEMENT OF TYPE 304L STAINLESS STEEL
Louthan, Jr., M. R., Donovan, J. A., and Rawl, Jr., D. E. (Du Pont de Nemours (E. I.) and Co., Aiken, SC)
Corrosion 29, No. 3, 108-111 (March 1973)

An experiment was conducted to determine the effect of high energy rate forging (HERF) and annealing on martensitic transformation and grain size of fractured tensile specimens of Type 304L stainless steel. Typical stress-strain curves are shown in this Technical Note. Hydrogen effects on tensile properties of the specimens are reported as is surface cracking of the test specimens. Extensive surface cracking and losses in ductility were observed in the fractured specimens of normal 304L exposed to hydrogen. Minimal effects were seen in the annealed HERF. It was concluded that a thermomechanical treatment of Type 304L stainless steel, which retards both the martensitic transformation and coplanar dislocation motion, appears to increase the resistance to SCC and hydrogen embrittlement. The investigators noted that more work needed to be done.

Important References:

1. Rhodes, P. R., Mechanisms of Chloride Stress Corrosion Cracking of Austenitic Stainless Steels, Corrosion 25, No. 11, 462 (November 1969).

2. Holzworth, M. L. and Louthan, Jr., M. R., Hydrogen-Induced Phase Transformations in Type 304L Stainless Steels, Corrosion 24, No. 4, 110-124 (April 1968).

3. Benson, Jr., R. B., Dann, R. K., and Roberts, Jr., L. W., Hydrogen Embrittlement of Stainless Steel, Trans. AIME 242, 2199-2205 (October 1968).

4. Vennett, R. M. and Ansell, G. S., Effect of High Pressure Hydrogen Upon Tensile Properties and Fracture Behavior of 304L Stainless Steel, Trans. ASM 60, 242-251 (June 1967).

Key words: Austenitic steels; dislocations (materials); ductile fracture; ductility; experimental data; hydrogen embrittlement; martensite; stainless steels; stress corrosion cracking.

ROLE OF HYDROGEN IN STRESS CORROSION CRACKING OF AUSTENITIC STAINLESS STEELS
Mehta, M. L. and Burke, J. (University Coll. of Swansea, Wales)
Corrosion 31, No. 3, 108-110 (March 1975)

The tensile properties of Types 304L and 310 austenitic stainless steels have been studied at 20° and 150°C (68° and 302°F) after cathodically charging with hydrogen at 100°C (212°F). The charging conditions were such as to avoid the complicating effects of hydrogen induced phase changes and surface cracking. It was found that a substantial decrease in ductility and flow stress was produced by the dissolved hydrogen. The implications of these results relative to the current controversy concerning the role of hydrogen in stress corrosion cracking (SCC) in the alloys is examined.

(FOR LISTING OF IMPORTANT REFERENCES, KEYWORDS AND A DUPLICATE ABSTRACT, SEE PAGE 44).

ANALYSIS OF THE INFLUENCE OF HYDROGEN ON PITTING CORROSION AND STRESS CORROSION OF AUSTENITIC STAINLESS STEEL IN CHLORIDE ENVIRONMENT

Seys, A. A., Brabers, M. J., and Van Haute, A. A., (Westinghouse Research Labs. Europe, Brussels, Belgium; Univ. Leuven, Haverlee, Belgium)

Corrosion 30, No. 2, 47-52 (February 1974).

In a study on the mechanism of pitting corrosion, a gas evolution in the pit has been observed. This gas has been gaschromatographically identified as hydrogen. The explanation of the evolution of hydrogen by the acidification of the pit electrolyte and the potential drop across the pit have been experimentally proved. By means of vacuum extraction experiments, the diffusion and dissolution of hydrogen in the metal has been shown. Experiments have been carried out to determine the effects of the dissolved hydrogen on the austenitic stainless steel. Replica techniques show that the hydrogen embrittles the metal around the pit. X ray diffraction lines demonstrate that hydrogen causes phase transformations in the austenitic stainless steel. In the case of pitting corrosion, such transformations have not yet been confirmed. It is suggested that dissolved hydrogen can create new initiation places for pitting corrosion and in this way is responsible for the secondary pit initiation. The most important effect of hydrogen is connected with the internal stresses set up in the metal. There is no hydrogen development during the pitting corrosion of pure nickel. This leads to the conclusion that hydrogen is not of primary importance in the pitting corrosion process. A comparison is made between the pitting and the stress corrosion process. The electrochemical processes occurring in both localized corrosion forms are analogous. The hydrogen is responsible for the cracking in the stress corrosion process. Stress corrosion cracking is represented as a specific case of pitting corrosion.

Important References:

1. Seys, A. A., Pitting Corrosion of Austenitic Stainless Steel in Chloride Environment, PhD Thesis, Univ. Leuven, Belgium (1972).

2. Brabers, M. J., Theory of Stress Corrosion Cracking in Alloys, NATO Science Committee (1971).

3. Brown, B. F., Theory of Stress Corrosion, NATO Science Committee (1971).

Key words: Environment effects; fracture analysis; hydrogen; pitting corrosion; polarization; stainless steels; stress corrosion; surface defects.

DUCTILITY LOSSES IN AUSTENITIC STAINLESS STEELS CAUSED BY HYDROGEN
Thompson, A. W. (Sandia Corp., Livermore, CA)
Proc. Int. Conf. Effects of Hydrogen on Material Properties and Selection and Structural Design, Champion, PA (23-27 September 1973).

It is important to understand the behavior of austenitic stainless steels in the presence of hydrogen since they are described as immune to hydrogen embrittlement. Research on four steels is summarized and the results are used to illustrate a mechanism for ductility losses in hydrogen. This mechanism involves dislocation transport of hydrogen and accumulation of the hydrogen at interfaces between the matrix and non-metallic inclusion particles. Fracture then occurs by normal, though accelerated, ductile rupture processes. In the case of A-286 steel, hydrogen behavior is somewhat different, as shown by fractographic changes in hydrogen tests.

Comment:

This paper also appears in Hydrogen in Metals, the ASM Materials/Metalworking Technology Series No. 2 (1974). A later, useful and relevant paper is Thompson's "The Mechanism of Hydrogen Participation in Ductile Fracture," presented at the International Conference on the Effect of Hydrogen on Behavior of Materials, Jackson Lake Lodge, Moran, WY, 7-11 September 1975.

The author in this series of papers has illustrated a potentially very important hydrogen effect. In these steels, though they remain nominally ductile, the hydrogen effect identified must be taken into account in design.

Important References:

1. Louthan, M. R., Caskey, G. R., Donovan, J. A., and Rawl, D. E., Hydrogen Embrittlement in Metals, Mater. Sci. Eng. 10, No. 6, 357-368 (December 1972).

2. Johnson, H. H., On Hydrogen Brittleness in High Strength Steels, in Fundamental Aspects of Stress Corrosion Cracking, NACE, Houston, TX (1969).

3. Tetelman, A. S., The Mechanism of Hydrogen Embrittlement in Steel, in Fundamental Aspects of Stress Corrosion Cracking, 446-460, NACE, Houston, TX (1969).

Key words: Austenitic steels; dislocations (materials); ductility; hydrogen embrittlement; ultimate strength; yield strength.

DIFFERENTIATING STRESS CORROSION CRACKING FROM HYDROGEN CRACKING OF FERRITIC 18-8 STAINLESS STEELS

Uhlig, H. H. and Newberg, R. T. (Massachusetts Inst. of Tech., Cambridge)

Corrosion 28, No. 9, 337-339 (September 1972).

An effect of rolling direction, supplementing the existence of a critical potential, can be employed to distinguish between hydrogen cracking and SCC of a ferritic or austenitic stainless steel. Hydrogen cracking can occur at room temperature, it is accelerated by cathodic polarization in many electrolytes, and it is sensitive to rolling direction. Stress corrosion cracking, by way of comparison, requires a specifically damaging anion like Cl-, it usually occurs only at elevated temperatures, susceptibility is independent of rolling direction, and damage can be avoided by cathodic protection.

Important References:

1. Elsea, A. R. and Fletcher, E. E., Hydrogen-Induced Delayed, Brittle Failures of High Strength Steels, DMIC Report 196 (1964).

2. Matsushima, I., Deegan, D., and Uhlig, H. H., Stress Corrosion and Hydrogen Cracking of 17-7 Stainless Steel, Corrosion 22, No. 1, 23-27 (1966).

3. Marquez, J., Matsushima, I., and Uhlig, H. H., Effect of Cold Rolling on Resistance of Ni-Fe Alloys to Hydrogen Cracking, Corrosion 26, No. 8, 215-222 (1970).

4. Uhlig, H. H. and Cook, Jr., E. W., Mechanism of Inhibiting Stress Corrosion Cracking of 18-8 Stainless Steel in $MgCl_2$ by Acetates and Nitrates, J. Electrochemical Soc. 116, No. 2, 173-177 (1969).

5. Wilde, B. E., Mechanism of Cracking of High Strength Martensitic Stainless Steels in Sodium Chloride Solution, Corrosion 27, No. 8, 326-333 (1971).

Key words: Anodic polarization; austenitic steels; cathodic polarization; cracking (fracturing); hydrogen embrittlement; stress corrosion.

IIID - Titanium Alloys

AN INVESTIGATION OF THE REACTION OF TITANIUM WITH HYDROGEN
Koehl, B. G., Hodge, W., and Williams, D. N. (Battelle Memorial Inst., Columbus, OH)
NASA CR-65456 (July 1966).

This summary report describes an investigation to determine whether titanium and titanium alloys could be made to react consistently with hydrogen at low temperatures and low to medium pressures. The work was undertaken in three phases characterized as follows: (1) pressurized H_2 environment with unstressed specimens; (2) pressurized H_2 environment with stressed specimens; and (3) experiments where unstressed specimens were enclosed in a special glass system design. Descriptions of the specimens and experimental procedures are detailed. Experimental data is included. Under pressure, but no stress, 10 of 86 Ti-50A specimens reacted in no apparent pattern. Under various constant and cycling loads at 300°F and 315 psia hydrogen, no reaction with Ti-50A was observed. It was shown that B120 VCA and Ti-6Al-4V were more reactive then Ti-50A and that Ti-5Al-2.5Sn was less reactive.

Important References:

1. Albrecht, W. M. and Bennett, R. E., Reaction of Hydrogen with Titanium at 300°F, Battelle Memorial Inst. Report (February 1957).

2. Williams, D. N. and Maykuth, D. J., Reaction of Hydrogen with Gaseous Hydrogen at Ambient Temperature, Battelle DMIC Technical Note (February 4, 1966).

3. Smith, D. P., Hydrogen in Metals, Univ. Chicago Press (1948).

Key words: Chemical reactions; hydrogen reaction embrittlement; hydrides; gas embrittlement; titanium alloys.

HYDROGEN EMBRITTLEMENT AND STRESS CORROSION CRACKING IN Ti-Al BINARY ALLOYS
Mauney, D. A., Starke, Jr., E. A., and Hochman, R. F. (Aluminum Co. of America, New Kensington, PA; Georgia Inst. of Tech., Atlanta)
Corrosion 29, No. 6, 241-244 (June 1973).

The fracture characteristics of hydrogen embrittlement (HE) in three binary Ti-Al alloys (2.5, 5, and 8 wt % Al) were investigated using electron fractography and x ray diffraction. The deformation characteristics of HE in these three alloys were also studied using thin foil transmission electron microscopy. A comparison was made between the HE and the stress corrosion cracking (SCC) fracture characteristics of these alloys. The similarities observed in SCC and HE failure in Ti-5 and 8 Al alloys strongly support the contention that hydrogen plays a significant role in the SCC process.

Important References:

1. Sanderson, G., Powell, D. T., and Scully, J. C., Stress Corrosion Cracking of Ti Alloys in Aqueous Chloride Solutions at Room Temperature, Corros. Sci. 8, No. 7, 473-481 (July 1968).

2. Sanderson, G. and Scully, J. C., Stress Corrosion of Ti Alloys in Methanolic Solutions, Corros. Sci. 8, No. 7, 541-548 (July 1968).

3. Powell, D. T. and Scully, J. C., Stress Corrosion Cracking of Alpha Titanium Alloys at Room Temperature, Corrosion 24, No. 6, 151-158 (June 1968).

Key words: Binary alloys; deformation; embrittlement; failures (materials); fractures (materials); hydrogen; material degradation; notched specimens; stress corrosion; stress intensity factor.

EFFECT OF HYDROGEN ON FRACTURE AND INERT-ENVIRONMENT SUSTAINED LOAD CRACKING RESISTANCE OF ALPHA-BETA TITANIUM ALLOYS
Meyn, D. A. (Naval Research Lab., Washington, DC)
Met. Trans. 5, 2405-2414 (November 1974)

The fracture toughness and resistance to inert-environment sustained load crack propagation of alpha-beta titanium alloys are usually reduced by increased hydrogen content. The range of hydrogen content over which fracture toughness or threshold stress intensity for sustained load cracking was observed to decrease when hydrogen content is small (0 to 50 ppm) for Ti-6Al-4V, but further increases in hydrogen content can cause an increase in cracking rates. Sustained load crack propagation is characterized by a mixture of microvoid coalescence with cleavage, usually on a plane 12 to 15 degrees from 0001 of the HCP alpha phase with some 0001 cleavage. Cleavage apparently initiates ahead of the main crack front within alpha grains, usually near apparent alpha-beta interfaces. Atmospheric moisture is inert with respect to sustained load cracking, that is, it does not cause stress corrosion cracking. Sustained load cracking was demonstrated in Ti-8Al-1V, Ti-6Al-6V-2Sn, and several grades of Ti-6Al-4V.

(FOR LISTING OF IMPORTANT REFERENCES, KEYWORDS AND A DUPLICATE ABSTRACT, SEE PAGE 53).

ENVIRONMENTAL HYDROGEN EMBRITTLEMENT OF AN α-β TITANIUM ALLOY: EFFECT OF MICROSTRUCTURE
Nelson, H. G., Williams, D. P., and Stein, J. E. (National Aeronautics and Space Administration, Ames Research Center, Moffett Field, CA)
Met. Trans. 3, 469-475 (February 1972).

Environmental hydrogen embrittlement of a Ti-6Al-4V alloy has been studied as a function of test displacement rate and of variations in α-β microstructure. Embrittlement in low pressure ($\sim$1 atm) gaseous hydrogen was inversely dependent on test displacement rate and strongly dependent on microstructure. At a given displacement rate, microstructures having a continuous α-phase matrix were less

severely embrittled than those having a continuous β-phase matrix. Further, brittle fracture occurred in the former microstructures by transgranular cleavage and in the latter microstructures by intergranular separation. These observations are consistent with previous studies made on slow strain-rate embrittlement of hydrogen-charged titanium alloys and are explained in terms of relative hydrogen transport rates within the α-phase and β-phase titanium.

(FOR LISTING OF IMPORTANT REFERENCES, KEYWORDS AND A DUPLICATE ABSTRACT, SEE PAGE 40).

THE ROLE OF HYDROGEN IN THE STRESS CORROSION CRACKING OF TITANIUM ALLOYS
Orman, S. and Picton, G. (Atomic Weapons Research Establishment, Aldermaston, England)
Corros. Sci. 14, 451-459 (July 1974)

Work with Ti-8Al-1Mo-1V has shown that the susceptibility of this alloy to stress corrosion cracking (SCC) in dilute saline solution is dependent on the hydrogen content of the material. Progressive removal of hydrogen results in increasing K_{IC} and K_{ISCC} until at about the 5 ppm level the material shows immunity to SCC. Addition of hydrogen also raises the level of the fracture toughness values of the material when tested in air or saline, but does not confer immunity to SCC. Removal of hydrogen has a similar effect on the fracture toughness properties of Ti-6Al-4V.

(FOR LISTING OF IMPORTANT REFERENCES, KEYWORDS AND A DUPLICATE ABSTRACT, SEE PAGE 45).

EFFECT OF HYDROGEN ON TITANIUM AND ITS ALLOYS
Paton, N. E. and Williams, J. C. (Rockwell International Science Center, Thousand Oaks, CA)
Proc. Int. Conf. on Effects of Hydrogen on Material Properties and Selection and Structural Design, Champion, PA (23-27 September 1973).

This paper presents a review of the behavior of hydrogen in titanium and titanium alloys. The influence of hydrogen concentration on the mechanical properties of titanium and its alloys is summarized. An attempt is made to interpret the observed property variations in concert with the existing level of understanding of the behavior of hydrogen in titanium. The results of investigations of the influence of gaseous hydrogen and stress corrosion inducing media on fracture behavior are described. The detrimental effect of hydrogen in titanium and its alloys is well known and in the early days of titanium production hydrogen induced failures were relatively frequent. The discussion of hydrogen effects in titanium is divided into those effects related to hydrogen already present in the material (internal hydrogen) either in solution or as hydrides, and those effects related to the interaction between titanium and hydrogen or hydrogen producing environments during service (external hydrogen). This paper adheres to this division of hydrogen effects; the first half contains a discussion of the behavior of internal hydrogen, including a discussion of the solubility of hydrogen in titanium and the morphology and habit planes of hydrides in titanium. The second part summarizes environmental effects including the possible role of hydrogen in hot salt and aqueous stress corrosion cracking of titanium and titanium alloys.

Comment:

This is a good summary paper which covers the empirical evidence for hydrogen effects in titanium. It is tutorial in nature and should be approached in that manner. The division of effects into internal or already present hydrogen and interaction with hydrogen in the environment is excellent from an engineering standpoint and will help to solve specific applications problems.

Important References:

1. Vitt, R. S. and Ono, K., Hydrogen Solubility in Alpha Titanium, Met. Trans. 2, 608-609 (1971).

2. Paton, N. E., Hickman, B. S., and Leslie, D. H., Behavior of Hydrogen in Alpha Phase Ti-Al Alloys, Met. Trans. 2, 2791-2796 (1971).

3. Cotterill, P., Hydrogen Embrittlement of Metals, Prog. Mater. Sci. 9, 265-301 (1961).

4. Van Leeuwen, H. P., A Quantitative Model of Hydrogen Induced Grain Boundary Cracking, Corrosion 29, 197-204 (1973).

5. Nelson, H. G., Environmental Hydrogen Embrittlement of an Alpha-Beta Titanium Alloy - Effect of Hydrogen Pressure, Met. Trans. 4, 364-367 (1973).

6. Gray, H. R., Ion and Laser Microprobes Applied to the Measurement of Corrosion Produced Hydrogen on a Microscopic Scale, Corrosion 28, 47-54 (February 1972).

Key words: Brittle fracture; crack growth rate; creep; diffusion; embrittlement; fractures (materials); hydrides; hydrogen reaction embrittlement; stress corrosion; subcritical crack growth; tensile strength; titanium alloys.

THE REACTION OF A TITANIUM ALLOY WITH HYDROGEN GAS AT LOW TEMPERATURES
Williams, D. N. and Wood, R. A. (Battelle Memorial Inst., Columbus, OH)
J. Less-Common Metals 31, 239-247 (1973)

An investigation of the effect of temperature on the surface hydriding reaction of Ti-5Al-2.5Sn alloy exposed to hydrogen at 250 psig was made. The temperature range studied extended from 160°F to -160°F. Reaction conditions were controlled so as to expose a vacuum-cleaned, oxide-free alloy surface to an ultra-pure hydrogen atmosphere. Reaction times up to 1548h were studied.

The hydriding reaction was extremely sensitive to experimental variables and the reproducibility of reaction behavior was poor. However, it was demonstrated that the reaction proceeded quite rapidly at 160°F; as much as 1 mil surface hydriding was observed after exposure for 162h. The amount of hydriding was observed to decrease with decreasing temperature at 75°F, -36°F, and -76°F. No surface hydriding was detected either by vacuum fusion analysis or by metallographic examination after exposure for 1458h at -110°F or -160°F. Tensile properties were unaffected by surface hydriding of the severity developed in this program (up to 1 mil thick) as determined by slow strain rate testing of hydrided sheet tensile samples.

(FOR LISTING OF IMPORTANT REFERENCES, KEYWORDS AND A DUPLICATE ABSTRACT, SEE PAGE 41).

IIIE - Nickel Alloys

THE INFLUENCE OF LOW PRESSURE HYDROGEN GAS ON CRACK GROWTH IN T.D.-NICKEL AND T.D.-NICHROME
Frandsen, J. D., Paton, N. E., and Marcus, H. L. (Rockwell International Science Center, Thousand Oaks, CA)
Scr. Met. 7, 409-414 (April 1973).

In this paper, fatigue crack propagation for thoria-dispersed (T.D.) nickel and nichrome is reported for a gaseous hydrogen environment (100 torr), vacuum (10^{-9} torr), and combined hydrogen and oxygen environment. Crack propagation rate was determined in three environments, and the fracture surfaces were examined using scanning electron microscopy and replica techniques. The experimenters concluded: (1) hydrogen interacts with T.D.-Nickel and Nichrome to increase cyclic crack growth rate; (2) the interaction is consistent with the observed lack of effect in hydrogen-charged T.D.-Nickel when the steady-state supply of hydrogen is considered.

Important References:

1. Pelloux, R. M., Mechanics of Formation of Ductile Fatigue Striations, Trans. ASM 62, 281 (1969).

2. Mostovoy, S., Crosley, R. P., and Ripling, E. J., J. Mater. 2, 661-681 (September 1967).

3. Walter, R. J. and Chandler, W. T., Effects of High Pressure Hydrogen on Metals at Ambient Temperature, NAR-Rocketdyne, Canoga Park, CA Report R-7780-1 (1969).

4. Marcus, H. L. and Stocker, P. J., AGARD Conf. Proc. No. 98, Stress Corrosion Testing Methods, Brussels, Belgium (1969).

5. Frandsen, J. D., Stocker, P. J., and Marcus, H. L., Fatigue Crack Propagation of Inconel 718 in Gaseous Environments, NAR Science Center Report SCTR-72-15 (1972).

Key words: Crack initiation; crack propagation; fatigue (materials); hydrogen embrittlement; nickel alloys.

THE INTERGRANULAR EMBRITTLEMENT OF NICKEL BY HYDROGEN: THE EFFECT OF GRAIN BOUNDARY SEGREGATION
Latanision, R. M. and Opperhauser, Jr., H. (Martin Marietta Labs., Baltimore, MD)
Met. Trans. 5, No. 2, 483-492 (February 1974).

The mechanical behavior of polycrystalline nickel specimens that were deformed in tension and cathodically charged with hydrogen simultaneously was investigated with particular emphasis on the fracture of such electrodes. This procedure leads to definite, if, however, weak serrated yielding and also markedly reduces the elongation at fracture compared to polycrystals unexposed to hydrogen. Moreover, in contrast to hydrogenated nickel monocrystals which neck down to give a chisel-edge fracture typical of ductile metals, hydrogenated polycrystal fractures are brittle and intergranular. The embrittlement of nickel by hydrogen is shown by means of Auger electron spectroscopy to be associated with the segregation of hydrogen recombination poisons to the grain boundaries. In essence, it is suggested that the entry of hydrogen into the nickel specimens occurs preferentially in the proximity of grain boundary intersections with the free surface, due to the presence therein of Sb and Sn which act as hydrogen recombination poisons and stimulate the absorption of hydrogen by the metal. The presence of such impurities in the grain boundaries suggests that a pressure mechanism is not involved in the intergranular cracking.

Comment:

This basic study provides one of the keys for the puzzle of hydrogen in nickel. The illumination of the segregation of the recombination poisons is significant in supporting a chemical rather than a pressure mechanism.

Important References:

1. Williams, D. P. and Nelson, H. G., Embrittlement of 4130 Steel by Low-Pressure Gaseous Hydrogen, Met. Trans. 1, 63-68 (1970).

2. Walter, R. J., Jewett, R. P., and Chandler, W. T., On the Mechanism of Hydrogen-Environment Embrittlement of Iron- and Nickel-Base Alloys, Mater. Sci. Eng. 5, 98-110 (1969/1970).

3. Louthan, Jr., M. R., Caskey, Jr., G. R., Donovan, J. A., and Rawl, Jr., D.E., Hydrogen Embrittlement of Metals, Mater. Sci. Eng. 10, No. 6, 357-368 (December 1972).

4. Oriani, R. A. and Josephic, P. H., Testing of the Decohesion Theory of Hydrogen-Induced Crack Propagation, Scr. Met. 6, No. 8, 681-688 (1972).

5. Shively, J. H., Hehemann, R. F., and Troiano, A. R., Hydrogen Permeability in a Stable Austenitic Stainless Steel Under Anodic Polarization, Corrosion 23, 215-217 (1967).

6. Shively, J. H., Hehemann, R. F. and Troiano, A. R., Hydrogen Permeability in a Stable Austenitic Stainless Steel Under Anodic Polarization, Corrosion 22, No. 9, 253-256 (September 1966).

7. Wilcox, B. and Smith, G. C., Intercrystaline Fracture in Hydrogen-Charged Nickel, Acta Met. 13, No. 3, 331-343 (1965).

8. Wilcox, B. and Smith, G. C., The Portevin-le-Chatelier Effect in Hydrogen Charged Nickel, Acta Met. 12, 371-376 (1964).

9. Latanision, R. M. and Staehle, R. W., The Effect of Continuous Hydrogenation in the Deformation of Nickel Single Crystals, Scr. Met. 2, 667-672 (1968).

Key words: Brittleness; ductility; grain boundaries; hydrogen embrittlement; microstructures; nickel alloys.

EFFECT OF HYDROGEN ON NICKEL AND NICKEL-BASE ALLOYS

Smith, G. C. (Cambridge Univ., England)

Proc. Int. Conf. on Effects of Hydrogen on Material Properties and Selection and Structural Design, Champion, PA (23-27 September 1973)

The paper discusses the effects which can be induced by hydrogen on the behavior of nickel and some of its alloys, and makes tentative proposals about their mechanism. The exact role played by hydrogen in reducing the ductility of nickel and some nickel alloys is not known but certain facts are now reasonably established: (A) hydrogen can interact with dislocations in nickel base materials and under certain conditions this can lead to an enhanced flow stress and rate of work hardening; (B) ductility is reduced by hydrogen in solution over a range of temperature which depends on the strain rate and type of test employed; (C) reduced ductility is usually accompanied by an increased proportion of intergranular failure; (D) some plastic deformation appears necessary as a preliminary to cracking and also for crack propagation; (E) the above effects can be observed at low overall concentrations of dissolved hydrogen; (F) embrittlement caused by external hydrogen coming from an atmosphere or from cathodic deposition, can occur even at high strain rates; (G) for a given composition heat-treatment can alter sensitivity to embrittlement. The evidence available does not enable a firm decision to be made about the mechanisms of embrittlement. The most significant points to be explained are the apparent need for some plastic deformation to initiate and continue cracking, the special role which the grain boundaries can play, the need for some localized concentration of hydrogen, the time-temperature nature of internal embrittlement and the role of an external hydrogen atmosphere.

Important References:

1. Windle, A. H. and Smith, G. C., The Effect of Hydrogen on the Deformation and Fracture of Polycrystalline Nickel, Metals Sci. J. 4, 136-144 (1970).

2. Wilcox, B. A. and Smith, G. C., The Portevin-le-Chatelier Effect in Hydrogen Charged Nickel, Acta Met. 12, 371-376 (1964).

3. Wilcox, B. A. and Smith, G. C., Intercrystaline Fracture in Hydrogen-Charged Nickel, Acta Met. 13, 331-343 (1965).

4. Walter, R. J. and Chandler, W. T., The Influence of Hydrogen Pressure and Notch Severity on Hydrogen Embrittlement, Mater. Sci. Eng. 8, 94-97 (1971).

5. Wayman, M. L. and Smith, G. C., Effects of Hydrogen on the Deformation and Fracture of Nickel-Iron Alloys, Acta Met. 19, 227-231 (1971).

6. Harris, J. A., Scarberry, R. C., and Stephens, C. D., Effects of Hydrogen on the Engineering Properties of Monel Nickel-Copper Alloy K-500, Corrosion 28, 57 (1972).

Key words: Dislocations (materials); ductility; fractures (materials); hydrides; hydrogen; hydrogen environment embrittlement; nickel alloys; stress-strain diagrams; yield strength.

EMBRITTLEMENT OF NICKEL-, COBALT-, AND IRON-BASE SUPERALLOYS BY EXPOSURE TO HYDROGEN

Gray, H. R. (National Aeronautics and Space Administration, Lewis Research Center, Cleveland, OH)

NASA TN-D-7805 (January 1975).

Five nickel alloys (Inconel 718, Udimet 700, Rene 41, Hastelloy X, and TD-NiCr), one cobalt-base alloy (L-605), and an iron-base alloy (A-286) were exposed in hydrogen at 15 psi at several temperatures in the range from 430°C to 980°C for as long as 1000 hours. These alloys were embrittled to varying degrees by such exposures in hydrogen. Embrittlement was sensitive to strain rate, was reversible, was caused by large concentrations of absorbed hydrogen, and was not associated with any detectable microstructural changes in the alloys. The observations are consistent with a mechanism of internal reversible hydrogen embrittlement.

Comment:

This empirical paper presents valuable information on the behavior of these materials. Further work is necessary to illuminate the mechanisms of these reversible embrittlements.

Important References:

1. Gray, H. R., Opening Remarks and Testing for Hydrogen Environment Embrittlement: Experimental Variables, in Hydrogen Embrittlement Testing, ASTM STP-543, 3-5 and 133-151 (1974).

2. Walter, R. J., Jewett, R. P., and Chandler, W. T., On the Mechanism of Hydrogen Environment Embrittlement of Iron- and Nickel-Base Alloys, Mater. Sci. Eng. 5, No. 2, 99-110 (January 1970).

3. Jewett, R. P., Walter, R. J., Chandler, W. T., and Frohmberg, R. P., Hydrogen Environment Embrittlement of Metals, NASA CR-2163 (1973).

4. Harris, Jr., J. A. and Van Wanderham, M. C., Properties of Materials in High Pressure Hydrogen at Cryogenic, Room, and Elevated Temperatures, NASA CR-124394 (1973).

5. Williams, D. P. and Nelson, H. G., Embrittlement of 4130 Steel by Low-Pressure Gaseous Hydrogen, Met. Trans. 1, No. 1, 63-68 (January 1970).

6. Bachelet, E. J. and Troiano, A. R., Hydrogen Gas Embrittlement and the Disc Pressure Test, NASA CR-134551 (1973).

Key words: Absorption; cobalt alloys; ductility; embrittlement; environment effects; gas embrittlement; heat resistant alloys; hydrogen; iron alloys; nickel alloys; residual strength; tensile tests.

HYDROGEN EMBRITTLEMENT OF HIGH STRENGTH FCC ALLOYS

Papp, J., Hehemann, R. F., and Troiano, A. R. (Case Western REserve Univ., Cleveland, OH)

Proc. Int. Conf. Effects of Hydrogen on Material Properties and Selection and Structural Design, Champion, PA (September 23-27, 1973).

The objective of the work reporred was to examine the sensitivity of several high strength FCC alloys to embrittlement by hydrogen charged electrolytically and to a smaller extent from the gaseous phase. It was shown that hydrogen charged K monel exhibits static delayed failure at temperatures in the range from 170°C to 260°C and low strain rate embrittlement at lower temperatures. Further, delayed failure of sample cathodically polarized while under stress have been observed in poisoned sulfric acid. A 286 exhibited SCC when exposed to LiCl at 130°C. As with lower strength stainless steels, a critical potential for cracking exists that is slightly cathodic to the rest potential. Hydrogen charged from the gas phase or electrolytically lowers the ductility of A 286 austenitic stainless steel.

Important References:

1. Whiteman, M. B. and Troiano, A. R., Hydrogen Embrittlement of Austenitic Steinless Steel, Corrosion 21, No. 2, 53-56 (February 1965).

2. Louthan, Jr., M. R., Donovan, J. A., and Rawl, Jr., D. E., Effect of High Dislocation Density on Stress Corrosion Cracking and Hydrogen Embrittlement of Type 304L Stainless Steel, Corrosion 29, No. 3 108-111 (March 1973).

3. Legrand, J., Caput, M., Conderec, C., Broudeur, R., and Fidelle, J. P., Contribution to the Study of Hydrogen Embrittlement in a STable Austenitic Steel, Mem. Sci, Rev. Met. 68, 861-869 (1971).

4. Fidelle, J. P., Broudeur, R., Porrovani, C., and Roux, C., Disk Pressure Technique, in ASTM STP-543, 34-47 (1974).

5. Dull, D. L., and Raymond, L., Surface Cracking of Inconel 718 During Cathodic Charging, Met. Trans. 4, 1635 (1973).

6. Harris, J. A., Scarberry, R. C., and Stephens, C. D., Effects of Hydrogen on the Engineering Properties of Monel Nickel Alloy K-500, Corrosion 28. 57 (1972).

Key words: Austenitic stainless steels; ductility; embrittlement; failure mode; gas embrittlement; hydrogen; hydrogen charging; strain rate.

THE EFFECTS OF HYDROGEN ON THE MECHANICAL PROPERTIES AND FRACTURE OF Zr AND REFRACTORY METALS
Birnbaum, H. K., Grossbeck, M. and Gahr, S. (Illinois Univ., Urbana)
AD-770235 (November 1973).

The effect of hydrogen on the mechanical properties of zirconium and the refractory metals is reviewed with particular attention paid to the effects on fracture and ductility. The various mechanisms proposed for the hydrogen embrittlement of these metals are reviewed. Both the effects of hydrogen in solution and in the surrounding gas phase are considered. New results on the embrittlement of Nb and Nb-N alloys obtained using a variety of experimental techniques are presented and discussed relative to the generic embrittlement phenomena in these metals. The relation of the crack propagation mechanism to stress and temperature induced phase changes is discussed and a model of hydrogen embrittlement is put forth.

Important References:

1. Oriani, R. A. and Josephic, P. H., Testing of the Decohesion Theory of Hydrogen-Induced Crack Propagation, Scr. Met. 6, No. 8, 681-688 (1972).

2. Birnbaum, H. K. and Wert, C., Berichte der Bunsen Gesell. für Phys. Chem. 76, 806 (1972).

3. Westlake, D. G., A Generalized Model for Hydrogen Embrittlement, Trans. ASM 62, No. 4, 1000-1006 (1969).

4. Westlake, D. G., Hydrogen Embrittlement: A Resistometric Study of Niobium (Columbium)-Hydrogen Alloys, Trans. AIME 245, 287 (1969).

5. Mueller, W. M., Blackledge, J. P. and Libowitz, G. G., Metal Hydrides, Academic Press, New York, NY (1968).

Key words: Cracking (fracturing); embrittlement; fractures (materials); hydrogen; mechanisms; refractory metals.

ROLE OF Hf AND Zr IN THE HYDROGEN EMBRITTLEMENT OF Ta AND Cb ALLOYS
Stephens, J. R. (National Aeronautics and Space Administration, Lewis Research Center, Cleveland, OH)
NASA TM-X-68293 (September 1973).

The discrete mechanisms of hydrogen embrittlement of various binary and ternary Ta and Cb alloys were investigated. The purpose of this paper is to characterize the hydrogen embrittlement of aged T-111 and similar Ta and Cb alloys and to describe the mechanisms believed responsible for the increased sensitivity of T-111 to low temperature hydrogen embrittlement after aging for 1000 hours or longer near 1040°C. A total of eight Ta base alloys and two Cb base alloys were investigated. The effects of pre-age annealing temperature, aging time, temperature and environment, and alloy composition on the susceptibility to hydrogen embrittlement were investigated. The primary method of determining the effects of these variables on the ductility of T-111 was by bend testing at 25° and -196°C. Fractured specimens were examined by the scanning electron microscope, electron microprobe, metallography and x ray diffraction.

Based on a study of the hydrogen embrittlement of aged Ta and Cb alloys the following conclusions were drawn:

1. Aging ternary Ta alloys such as T-111 (Ta-8W-2Hf) near 1040°C for 1000 hours or longer increases their sensitivity to low temperature hydrogen embrittlement.

2. Segregation of Hf to grain boundaries during aging causes embrittlement upon testing at -196°C and is responsible for the observed hydrogen embrittlement.

3. Binary Ta and Cb alloys, Ta-2Hf and Cb-1Zr, are not susceptible to hydrogen embrittlement under the conditions of this study and did not exhibit grain boundary segregation of Hf or Zr.

4. Ternary alloys Ta-8W-.5Hf, Ta-8W-1Hf, and Ta-4W-2Hf are superior to T-111 for containment of alkali metals in that they do not exhibit aging embrittlement. However, these alloys in the aged condition are susceptible to hydrogen embrittlement. Binary alloys Ta-2Hf and Cb-1Zr are attractive containment materials based on retention of low temperature ductility after aging and hydrogen doping; however, their relatively low tensile strengths at 1040°C may limit their use.

Important References:

1. Moss, T. A., Davies, R. L., and Barna, G. J., NASA SP-245 (1970).

2. Watson, G. K. and Stephens, J. R., NASA TN-D-6988 (1972).

Key words: Grain boundaries; hydrogen embrittlement; microstructures; niobium alloys; refractory metals; tantalum alloys; tensile strength.

HYDROGEN EMBRITTLEMENT OF ALUMINUM ALLOYS
Speidel, M. O. (Brown, Boveri and Co., Ltd., Baden, Switzerland)
Proc. Int. Conf. Effects of Hydrogen on Material Properties and Selection and Structural Design, Champion, PA (September 23-27, 1973).

This paper reviews the conditions under which hydrogen embrittlement of aluminum alloys is - or is not - observed. It is shown that aluminum alloys can be reversibly embrittled by diffusible hydrogen driven into the lattice when the environing fugasity is high. Hydrogen embrittlement of aluminum alloys can cause intergranular crack growth. Stress corrosion cracking of aluminum alloys in water vapor containing gases can be attributed to hydrogen embrittlement. Stress corrosion cracking of aluminum alloys in aqueous solutions could be due to hydrogen. Dry gaseous hydrogen does not cause any significant hydrogen embrittlement in aluminum alloys. A number of unsolved questions are presented for future research including: what is the effect or microstructure and heat treatment of aluminum alloys on hydrogen embrittlement; is discontinuous crack growth really a feature intrinsically associated to hydrogen embrittlement of aluminum alloys (or hydrogen embrittlement in general) as many researchers claim; and what is the role of plastic deformation in hydrogen embrittlement of aluminum alloys:

Comment:

The author has presented a thoughtful discussion of the problems of identifying the role of hydrogen in the embrittlement of aluminum alloys. This paper asks some searching questions for future research both experimental and theoretical.

Important References:

1. Wei, R. P., Fatigue-Crack Propagation in High Strength Aluminum Alloy, Int. J. Fract. Mech. 4, 155-170 (1968).

2. Nelson, H. G., The Kinetic and Mechanical Aspects of Hydrogen-Induced Failure in Metals, NASA Technical Note D-6691 (1972).

3. Gest, R. and Troiano, A. R., Environmental Induced Failure of a High Strength Aluminum Alloy, PhD Thesis of R. Gest, Case Western Reserve Univ. (1972).

4. Haynie. F. H. and Boyd, W. K., Electroehcmical Study of the Mechanism of Stress Corrosion Cracking in an Aluminum-Zinc-Magnesium Alloy, in Fundamental Aspects of Stress Corrosion Cracking, 580-589, NACE, Houston, TX (1969).

Key words: Aluminum alloys; crack growth rate; diffusion; embrittlement; fractures (materials); humidity; hydrogen; hydrogen charging; stress corrosion; stress intensity factor; subcritical crack growth.

IVA - Characterization

HYDROGEN GAS EMBRITTLEMENT AND THE DISC PRESSURE TEST
Bachelet, E. J. and Troiano, A. R. (Case Western Reserve Univ., Cleveland, OH)
NASA CR-134551 (November 30, 1973).

A disc pressure test was used to study the influence of a hydrogen gas environment on the mechanical properties of three high strength superalloys, Inconel 718, L-605, and A-286, in static and dynamic conditions. The influence of the hydrogen pressure, loading rate, temperature, and mechanical and thermal fatigue was investigated and reported. The permeation characteristics of Inconel 718 was determined in collaboration with the French AEC. The results complemented by a fractographic study proved consistent with a stress-sorption or an internal embrittlement type of mechanism.

Important References:

1. Gray, H. R., Testing for Hydrogen Environment Embrittlement: Experimental Variables, in Hydrogen Embrittlement Testing, ASTM STP-543, 133-151 (1974).

2. Boniszewski, T. and Smith, G. C., The Influence of Hydrogen on the Plastic Deformation, Ductility, and Fracture of Nickel, Acta Met. 11, 165 (1963).

3. Nelson, H. G., Williams, D. P., and Tetelman, A. S., Embrittlement of a Ferrous Alloy in a Partially Dissociated Hydrogen Environment, Met. Trans. 2, No. 4, 953-959 (April 1971).

4. Fidelle, J. P., Quick Pressure Hydrogen Embrittlement Test of Metal Discs, Colloquium Hydrogen in Metals, Valduc, Edited by Le Centre D'Etudes de Bruyeres - le - Chatel, 91 France, 131 (September 1967).

5. Hancock, G. G. and Johnson, H. H., Hydrogen, Oxygen and Subcritical Crack Growth in a High Strength Steel, Trans. AIME 236, No. 4, 513-516 (April 1966).

6. Peterson, J. A., Gibala, R., and Troiano, A. R., Hydrogen Induced Embrittlement and Internal Friction in Stable Austenitic Steel, Congress Hydrogen in Metals, Valduc Colloquium, 200 (September 1967).

Key words: Cobalt alloys; disc pressure tests; gas embrittlement; hydrogen embrittlement; iron alloys; mechanisms; nickel alloys; strain rate; tensile tests.

MECHANICAL TESTING METHODS
Groeneveld, T. P. and Elsea, A. R. (Battelle Columbus Labs., OH)
Hydrogen Embrittlement Testing, ASTM STP-543, 11-19 (1974)

An experimental approach and experimental procedures for evaluating the hydrogen-stress cracking (HSC) of steels as a result of hydrogen absorbed during processing or service are described. The procedures involve sustained loading of specimens while they are being charged with hydrogen under conditions that provide hydrogen entry rates or result in hydrogen contents representative of those obtained from processing or service environments. The procedure can be used to evaluate the relative susceptibilities of various steels to HSC or to evaluate the tendencies for processing or service environments to cause HSC in steels.

Important References:

1. Elsea, A. R. and Fletcher, E. E., Hydrogen-Induced, Delayed, Brittle Failures of High Strength Steels, DMIC Report 196, Battelle Labs. (January 20, 1964).

2. Groeneveld, T. P., Fletcher, E. E., and Elsea, A. R., A Study of Hydrogen Embrittlement of Various Alloys, Final Report, NASA Contract NAS8-20029 (January 23, 1969).

Key words: Cathodic polarization; cracking (fracturing); fractures (materials); hydrogen charging; hydrogen embrittlement; stress corrosion cracking; test procedures.

TENSILE AND FRACTURE PROPERTIES OF AUSTENITIC STAINLESS STEEL 21-6-9 IN HIGH PRESSURE HYDROGEN GAS
Vandervoort, R. R. (California Univ., Livermore. Lawrence Livermore Lab.)
Metals Eng. Quart. 12, 10-16 (February 1972).

The purpose of this study was to determine if 21-6-9 is susceptible to embrittlement in high-pressure hydrogen gas. Tensile, fracture, and static load tests were performed on both base and weld metal (composition: 0.03C, 8.8Mn, 0.01P, 0.003S, 0.4Si, 7.1Ni, 21.0Cr, 0.03Mo, 0.08Co, 0.07 Cu, 0.3N, 2ppm H).

The results of the study are summarized as follows:

(1) Data from tensile, notch tensile, static load, and fracture tests as well as post-test examination of microstructures by fractography and metallography showed that base metal and welded 21-6-9 stainless steel are apparently not susceptible to embrittlement by high-pressure hydrogen gas. The probability of failure for 21-6-9 due to effects of high-pressure hydrogen is low.

(2) The yield strength of 21-6-9 in air, 10,000 psi helium, and 10,000 psi hydrogen was about 80,000 psi. Elongations were around 50 pct, and reduction of areas was around 65 pct. Ductility was independent of the test environment. The alloy has good work-hardening characteristics.

(3) Tensile properties of TIG and EB welds were unaffected by a high-pressure hydrogen environment. Weld efficiencies based on yield strength were 95 pct or greater. Reduction of area for both types of welds was around 70 pct, and elongation of specimens containing welds was about 12 pct.

(4) Both base metal and weld metal had good notch ductilities and were not notch sensitive.

(5) The apparent fracture toughness of base metal and welded 21-6-9 in H_2, He, and air test environments was about 100 ksi $\sqrt{in.}$

Important References:

1. Hofmann, W. and Rauls, W., Ductility of Steel Under Influence of External High Pressure Hydrogen, Weld. J. Res. Suppl. 44, No. 5, 225S-230S (1965).

2. Steinman, J. B., Van Ness, H. C. and Ansell, G. S., Effect of High-Pressure Hydrogen Upon Notch Tensile Strength and Fracture Mode of 4140 Steel, Weld. J. Res. Suppl. 44, No. 5, 221S-224S (1965).

3. Vennett, R. M. and Ansell, G. S., Effect of High Pressure Hydrogen Upon Tensile Properties and Fracture Behavior of 304L Stainless Steel, Trans. ASM 60, No. 2, 242-251 (1967).

4. Benson, Jr., R. B., Dann, R. K., and Roberts, Jr., L. W., Hydrogen Embrittlement of Stainless Steel, Trans. AIME 242, No. 10, 2199-2205 (1968).

5. Davidson, T. E., Uy, J. C., and Lee, A. P., Tensile Fracture Characteristics of Metals Under Hydrostatic Pressures to 23 Kilobars, Acta Met. 14, No. 8, 937-948 (1966).

6. Davidson, T. E. and Ansell, G. S., Structure Sensitivity of Effects of Pressure Upon Ductility of Fe-C Materials, Trans. ASM 61, No. 2, 242-254 (1968).

Key words: Austenitic steels; cracking (fracturing); delayed failure; ductility; elongation; fracture strength; gas embrittlement; hydrogen embrittlement; microstructure; stainless steels.

TESTING FOR HYDROGEN ENVIRONMENT EMBRITTLEMENT: EXPERIMENTAL VARIABLES
Gray, H. H. (National Aeronautics and Space Administration, Lewis Research Center, Cleveland, OH)
Hydrogen Embrittlement Testing, ASTM STP-543, 133-151 (1974).

Hydrogen embrittlement is classified into three types: (1) internal reversible hydrogen embrittlement; (2) hydrogen reaction embrittlement; and (3) 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, gas purity, strain rate, stress concentration factor, and test temperature are discussed. Additional research is required to determine whether hydrogen environment embrittlement are similar or distinct types of embrittlement.

(FOR LISTING OF IMPORTANT REFERENCES, KEYWORDS AND A DUPLICATE ABSTRACT, SEE PAGE 19).

PROPERTIES OF MATERIALS IN HIGH PRESSURE HYDROGEN AT CRYOGENIC, ROOM, AND ELEVATED TEMPERATURES
Harris, Jr., J. A., and Van Wanderham, M. C. (Pratt and Whitney Aircraft, West Palm Beach, FL)
NASA CR-119884 (June 30, 1971)

This report describes experiments which included mechanical property tests of nickel-base, titanium-base, and iron-base alloys in 5000 psig gaseous helium and hydrogen at various temperatures, and the comparison of test results to determine degradation of properties due to the hydrogen environment. Data was tabulated on low cycle fatigue, high cycle fatigue, fracture toughness, creep rupture, and tensile properties in high pressure hydrogen. A system was established comparing the properties in helium as a baseline to those in hydrogen. It was shown that for the conditions and materials tested the most severe tests of a material for hydrogen degradation are creep rupture and low cycle fatigue, followed in order by high cycle fatigue, tensile and fracture toughness tests.

Key words: Creep rupture; ductility; elongation; embrittlement; fatigue properties; heat resistant alloys; hydrogen environment embrittlement; iron alloys; nickel alloys; plastic properties; tensile properties; titanium alloys.

NEODYMIUM DETECTION SYSTEM
Toy, S. M. (Lockheed Missiles and Space Co., Palo Alto, CA)
Hydrogen Embrittlement Testing, ASTM STP-543, 124-130 (January 1974).

A test method for assessing hydrogen embrittlement of high strength steel parts in the field is described. It is applicable to both ferrous and nonferrous metals which evolve hydrogen when heated. The assessment of the hydrogen embrittlement of steel or other metal parts is dependent on the determination of the local hydrogen content and the stresses required to fracture them and the determination of the hydrogen pick-up rate by the metal part in the environment to which it is exposed. Local hydrogen analysis in the field is based on the application of a flexible neodymium hydrogen detection tape.

Important References:

1. Toy, S. M. and Phillips, A., Hydrogen Emanation and Distribution in Metals and Alloys, Corrosion 26, No. 7, 200-207 (July 1970).

2. Fletcher, E. E. and Elsea, A. R., Hydrogen Movement in Steel, - Entry, Diffusion, and Elimination, DMIC Report 219 (June 1965).

3. Sink, G. T., Hydrogen Embrittlement of High-Strength Steels, McDonnell Douglas Paper 5377 (June 30, 1969).

Key words: Analysis methods; detection systems; embrittlement; fractures (materials); high strength steels; hydrogen; stress corrosion.

DEVELOPMENT OF A NUCLEAR MICROPROBE TECHNIQUE FOR HYDROGEN ANALYSIS IN SELECTED MATERIALS
Padawer, G. M. and Adler, P. N. (Grumman Aerospace Corp., Bethpage, NY)
AD-770856 (1973)

The lithium nuclear microprobe (LNM) for the measurement of hydrogen concentration depth profiles in material surfaces was studied. The determination of acceptable hydrogen concentration standards, the optimization of hydrogen detection sensitivity, and the establishing of the relationship between probing depth and bombarding energy is described. The hydrogen concentration calibration was performed using hydrogen-in-titanium NBS standards and Kapton, a polymide film. The LNM technique was also applied to specific material problems. Hydrogen surface concentrations were measured in cadmium and chromium plated D6AC steel samples, smooth and fractured Ti-6Al-4V surfaces that had been exposed to a stress corrosion environment, and smooth surfaces of 7075 aluminum alloys that had been exposed to conditions of stress corrosion. Hydrogen concentration depth profiles were measured in cadmium plated D6AC steel and 7075 aluminum alloy samples. Very high hydrogen concentrations found in these samples were linked to mechanical property degradation and corrosion.

Comment:

The experiment results described in this paper tend to identify the LNM as a tested, currently unmatched, diagnostic technique for accurate in situ measurements of localized hydrogen concentrations.

Important References:

1. Rogers, H. C., Hydrogen Embrittlement of Metals, Science 159, 1057-1064 (1968).

2. Groenveld, T. P., Fletcher, E. E., and Elsea, A. R., Review of Literature on Hydrogen Embrittlement, Contract NAS 8-20029 (January 12, 1966).

3. Walter, R. J. and Chandler, W. T., Effects of High Pressure Hydrogen on Metals at Ambient Temperature, Final Report, Contract NAS 8-19 (February 28, 1969).

4. Walter, R. J., Jewett, R. P., and Chandler, W. T., On the Mechanism of Hydrogen-Environment Embrittlement of Iron- and Nickel-Base Alloys, Mater. Sci. Eng. 5, 98-110 (1969).

5. Campbell, J. E., Effects of Hydrogen Gas on Metals at Ambient Temperature, DMIC Report S-32 (April 1970).

6. Gray, H. R., Ion and Laser Microprobe Applied to the Measurement of Corrosion-Produced Hydrogen on a Microprobe Scale, Corrosion 28, 47-54 (1972).

Key words: Aluminum alloys; analysis methods; detection systems; embrittlement; hydrogen; material degradation; NDT methods; quantitative analysis.

THE USE OF ACOUSTIC EMISSION TESTING TO MONITOR HYDROGEN EMBRITTLEMENT IN STEELS
Tetelman, A. S. (California Univ., Los Angeles)
Proc. Third Tewksbury Symp. Fracture, Effects of Chemical Environments on Fracture Processes, Melbourne Univ., Australia (4-6 June 1974).

Acoustic emission is identified as a relatively new method of non-destructive inspection that can be used to monitor microcrack formation and crack growth. The principles of acoustic emission are discussed. Recent models of hydrogen embrittlement are then presented and related to fracture mechanics parameters. The two concepts are then combined and the acoustic emission accompanying hydrogen cracking is discussed. Particular emphasis is given to cathodically charged specimens and components and to welded specimens in which the hydrogen is introduced during the welding process. The use of acoustic emission to monitor plating baths is described. Finally, some discussion of the use of acoustic emission as a tool for studying hydrogen cracking is presented.

Important References:

1. Dunegan, H. L. and Tetelman, A. S., Nondestructive Characterization of Hydrogen Embrittlement Cracking by Acoustic Emission Techniques, Eng. Fract. Mech. 2, 387-402 (1971).

2. Tiner, N. A. and Gilpin, C. B., Microprocesses in Stress Corrosion of Martensitic Steels, Corrosion 22, No. 10, 271-279 (1966).

3. Tetelman, A. S. and Robertson, W. D., Mechanism of Hydrogen Embrittlement Observed in Iron-Silicon Single Crystals, Trans. AIME 224, No. 4, 775-783 (1962).

4. Wilshaw, T., Rau, C. A., and Tetelman, A. S., General Model to Predict Elastic-Plastic Stress Distribution and Fracture Strength of Notched Bars in Plane Strain Bending, Eng. Fract. Mech. 1, No. 1, 191-211 (1968).

Key words: Acoustic emission; analysis methods; crack detection; crack propagation; detection systems; hydrogen charging; hydrogen environment embrittlement; NDI methods; NDI techniques; stress corrosion cracking; subcritical crack growth.

ACOUSTIC EMISSIONS AND STRESS-CORROSION CRACKING IN HIGH-STRENGTH ALLOYS
Tucker, T. R. and Fujii, C. T. (Naval Research Lab., Washington, DC)
AD-785009 (August 1974).

The usefulness of acoustic emission data; i.e., stress wave emission (SWE) to studies of stress-corrosion cracking (SCC) of high strength alloys was explored. Single-edge-notched, precracked, cantilever specimens were used to study the stress-corrosion-crack growth and SWE characteristics of a high strength stainless steel and a titanium alloy. SWE data correlate reasonably well with crack growth measurements by conventional beam deflection techniques for high-strength stainless steel but are too insensitive for reliable detection of crack extension in the titanium alloy. The use of SWE data to define the energetics of discrete cracking events are currently beyond the capabilities of existing equipment and analytics.

Important References:

1. Tetelman, A. S., Acoustic Emission and Fracture Mechanics Testing of Metals and Composites, UCLA - Eng - 7249 (1972).

2. Engle, R. B., Dunegan, H. L., Acoustic Emission: Stress-Wave Detection as a Tool for Nondestructive Testing and Material Evaluation, Int. J. Nondestruct. Test. 1, 109 (1969).

3. Dunegan, H. L. and Green, A. T., Factors Affecting Acoustic Emission Response from Materials, Mater. Res. Stand. 11, No. 3, 21 (1971).

4. Hartbower, C. E., Reuter, W. G., and Crimmins, P. P., Mechanisms of Slow Crack Growth in High Strength Steels and Titanium, AFML-TR-67-26 (1969).

5. Beachem, C. D., A New Model for Hydrogen Assisted Cracking, Met. Trans. 3, 437 (1972).

6. Radon, J. C., and Pollock, A. A., Acoustic Emissions and Energy Transfer During Crack Propagation, Eng. Fract. Mech. 4, 295 (1972).

Key words: Acoustic emission; analysis tools; crack growth rate; crack propagation; detection systems; fracture mechanics; NDE techniques; NDT techniques; stainless steels; stress corrosion; stress corrosion cracking; stress wave emission; titanium alloys.

STRESS-CORROSION CRACK DETECTION AND CHARACTERIZATION USING ULTRASOUND
Weil, B. L. (Lockheed-Georgia Co., Marietta)
Mater. Eval. 27, No. 6, 135-139, 144 (June 1969)

Stress-corrosion cracking is a complicated mechanism involving: (1) sustained surface tensile stresses; (2) an alloy and temper susceptible to this phenomenon; and (3) a corrosive atmosphere. Described is the development of a nondestructive test technique following the occurrence of a stress-corrosion failure in a ring support structure of 7075-T6. Configuration of the part and concealment of the area of surface tensile stresses under a glass-resin structure dictated that a shear wave technique be used to detect and characterize the stress-corrosion cracks. Test frequencies, types of search unit, and various complaints were investigated to determine optimum sensitivity and resolution with minimum attenuation. Test techniques were developed with concern for location of probe, angle of refracted wave, and amplitude of discontinuity indication. To simulate discontinuities, machined standards with areas related to cracks of various locations, sizes, depth, and angles were evaluated. Characterization was finally optimized through development of standards with induced stress-corrosion cracks of various sizes, locations, depth and angles propagated by submitting sections of the part to acidified salt spray while under a residual tensile stress of 80 percent of the yield stress. Information was correlated using data from both the ultrasonic and metallographic evaluation of these specimens.

Key words: Analysis tools; aluminum alloys; corrosion; cracking (fracturing); detection systems; inspection procedures; inspection standards; NDT methods; stress corrosion cracking; ultrasonic imaging; ultrasonic tests.

TESTING OF THE DECOHESION THEORY OF HYDROGEN-INDUCED CRACK PROPAGATION
Oriani, R. A. and Josephic, P. H. (United States Steel Corp., Monroeville, PA)
Scr. Met. 6, No. 8, 681-688 (1972).

This paper describes experiments designed and carried out to test the decohesion theory of hydrogen assisted crack growth. The results were consistent with the demands of the decohesion theory. This theory is that at the threshold value of hydrogen pressure at a given stress intensity factor one has not only a mechanical but also a chemical (unstable) equilibrium between the specimen and its mechanical and chemical environment. This means that a very slight increase in pressure should produce a finite crack velocity. The restarting of a self-arrested crack by very small hydrogen pressure increments is a natural consequence of the decohesion theory.

Comment:

The critical experiment described in this paper relating to restarting crack growth resulting from small increments in the ambient hydrogen gas pressure was one of the significant factors in giving support to the decohesion postulate. The discussion by the authors of the uniqueness of this result is quite adequate and has been extensively referred to by other authors.

Important References:

1. Novak, S. R. and Rolfe, S. T., Modified WOL Specimen for K_{ISCC} Environmental Testing, J. Mater. 4, No. 3, 701-728 (1969).

2. Hancock, G. G. and Johnson, H. H., Hydrogen, Oxygen, and Subcritical Crack Growth in a High Strength Steel, Trans. AIME 236, No. 4, 513 (1966).

Key words: Crack initiation; crack propagation; decohesion; fracture tests; hydrogen embrittlement; laboratory tests; models; stress intensity factor; theories.

EQUILIBRIUM ASPECTS OF HYDROGEN-INDUCED CRACKING OF STEELS
Oriani, R. A. and Josephic, P. H. (United States Steel Corp., Monroeville, PA)
Acta. Met. 22, 1065-1074 (September 1974).

The threshold pressures of hydrogen and of deuterium gases necessary to cause crack propagation in AISI 4340 of 250 psi yield strength have been determined as a function of plane strain stress intensity factor at room temperature. The functional threshold pressure is shown to be well fitted by an analytical expression derived from the unstable equilibrium form of the decohesion theory plus some reasonable ad hoc assumptions for the necessary functional relationships. From the fitting of the theoretical equation to the experimental data are obtained numerical values for the hydrostatic component of the stress at the crack front, for the equilibrium enhancement of concentration of hydrogen, and for the reduction by the hydrogen of the maximum cohesive resistive force. The magnitudes of these numbers and their trends with plane strain stress intensity factor are in agreement with expectations from the decohesion theory but with no other extant point of view.

(FOR LISTING OF IMPORTANT REFERENCES, KEYWORDS AND A DUPLICATE ABSTRACT, SEE PAGE 62).

THE EFFECT OF LOADING MODE ON HYDROGEN EMBRITTLEMENT
St. John, C. and Gerberich, W. W. (California Univ., Berkeley)
Met. Trans. 4, 589-594 (February 1973).

Hydrogen embrittlement is shown to occur very easily in notched-round bars under opening mode I (tension) but not under antiplane shear mode III (torsion). The stress tensor invariants under mode I, II, and III loadings and how these affect interstitial diffusion are discussed. It is suggested that long range diffusion of hydrogen down orthogonal trajectories to the vicinity of the crack tip, which can occur under mode I but not mode III, is a key part of any hydrogen embrittlement mechanism. This premise was evaluated with AISI 4340 steel heat treated to ultrahigh strength levels. It was found that an initial mode I stress intensity level of 17,000 psi-in$^{1/2}$ produced failure in several minutes. Mode III stress intensity levels three times this produced no crack initiation in 300 min. Further analysis of the time-dependent hydrogen concentrating effect utilized a stress wave emission technique. This produced plausible critical hydrogen concentrations even though the present elastic analysis is a first order approximation of the stress field.

Comment:

The authors have conducted a critical experiment which proves the necessity for cubic dilatation at the crack tip to provide the driving force for hydrogen transport. Additional experiments are needed on other alloys to further establish this transport mechanism. Additional experiments are also necessary to determine the function of the hydrogen in extending the crack.

Important References:

1. Barth, C. F. and Steigerwald, E. A., Evaluation of Hydrogen Embrittlement Mechanisms, Met. Trans. 2, 1988 (1971).

2. Liu, H. W., Stress Corrosion Cracking and the Interaction Between Crack-Tip Stress Field and Solute Atoms, J. Basic Eng. 92, 633 (September 1970).

3. Barth, C. F. and Steigerwald, E. A., Evaluation of Hydrogen Embrittlement Mechanisms, Met. Trans. 1, 3451-3455 (1970).

4. Paris, P. C. and Sih, G. C., Stress Analysis of Cracks, in Fracture Toughness Testing and Its Applications, ASTM STP-381 (April 1965)

5. Wilson, W. K., Clark, Jr., W. G., and Wessel, Fracture Mechanics Technology for Combined Loading and Low-to-Intermediate Strength Metals, Westinghouse Report, Contract CAAE 07-67-C-4021 (November 1968).

Key words: Analysis methods; diffusion; hydrogen embrittlement; load distribution (forces); stress intensity factor.

A QUANTITATIVE MODEL OF HYDROGEN INDUCED GRAIN BOUNDARY CRACKING
Van Leeuwen, H. P. (National Aerospace Lab., Amsterdam, Netherlands)
Corrosion 29, No. 5, 197-204 (May 1973)

Equations are developed describing the diffusion to and the subsequent precipitation of hydrogen into lenticular voids resulting from the stress induced decohesion and grain boundary precipitates. Cracking is treated in terms of the fracture mechanics related to an embedded lenticular flaw loaded by an internal pressure and a gross section stress. The author concludes that: (1) stress induced decohesion of grain boundary precipitates may produce planar voids that will serve as precipitation sites of hydrogen dissolved in the metal lattice; (2) hydrogen concentrations may be high locally due to the tendency of hydrogen to diffuse to and accumulate at sites with high triaxial stresses; (3) if the local concentration is a multiple of the normal solubility, Sieverts' law predicts high pressures of the hydrogen in the voids; (4) grain boundary cracking can be predicted on the basis of the Barenblatt solution for the stress intensity factor at an embedded lenticular crack loaded by an internal pressure and a gross section stress; (5) this model of hydrogen induced grain boundary cracking could apply to a variety of alloys besides steels; (6) the model predicts that there will be a ratio of grain boundary particle size to spacing associated with maximum susceptibility to cracking.

Important References:

1. Chew, B., A Void Model for Hydrogen Diffusion in Steel, J. Metal Sci. 5, 195 (1971).

2. Van Leeuwen, H. P., A Quantitative Model of Hydrogen Induced Grain Boundary Cracking, NLR TR-72024-C (1972).

3. Bernstein, I. M., The Role of Hydrogen in the Embrittlement of Iron and Steel, Mater. Sci. Eng. 6, 1 (1970).

4. Evans, G. M. and Rollason, C., Influence of Nonmetallic Inclusions on the Apparent Diffusion of Hydrogen in Ferrous Materials, J. Iron Steel Inst. 207, 1484 (1969).

Key words: Analysis methods; crack analysis; decohesion; diffusion; dislocations (materials); embrittlement; grain boundaries; hydrogen; models; quantitative analysis; stress intensity factor; theories.

A GENERALIZED MODEL FOR HYDROGEN EMBRITTLEMENT
Westlake, D. G. (Argonne National Lab., IL)
Trans. ASM 62, 1000-1006 (1969).

A generalized model for hydrogen embrittlement is proposed. The model is based on the premise that hydrogen embrittlement of any metal can be explained in terms of localized formation of a phase whose mechanical properties differ from those of the matrix because of hydrogen enrichment. Both endothermic and exothermic occluders of hydrogen are discussed and it is argued that previously proposed, seemingly conflicting models are not incompatible. Some consequences of the model are suggested and experimental evidence is presented to justify the model.

Important References:

1. Westlake, D. G., The Combined Effects of Oxygen and Hydrogen on the Mechanical Properties of Zirconium, Trans. AIME 233, 368 (1965).

2. Westlake, D. G., Hydrogen Embrittlement: A Resistometric Study of Niobium (Columbium) - Hydrogen Alloys, Trans. AIME 245, 287 (1969).

3. Wood, T. W. and Daniels, R. D., The Influence of Hydrogen on the Tensile Properties of Columbium, Trans. AIME 233, 898 (1967).

4. Longson, B., The Hydrogen Embrittlement of Niobium, TRG Report 1035 (January 1966).

5. Westlake, D. G., Mechanical Behavior of Niobium-Hydrogen Alloys, Trans. AIME 245, 1969 (1969).

6. Sherman, D. H., Owen, C. V., and Scott, T. E., The Effect of Hydrogen on the Structure and Properties of Vanadium, Trans. AIME 242, 1775 (1968).

Key words: Ductility; failure mechanisms; hydrides; hydrogen embrittlement; material degradation; models; theories.

THE COOPERATIVE RELATION BETWEEN TEMPER EMBRITTLEMENT AND HYDROGEN EMBRITTLEMENT IN HIGH STRENGTH STEEL
Yoshino, K. and McMahon, Jr., C. J. (Kamaishi Works, Nippon Steel Corp., Kamaishi, Iwate, Japan; Pennsylvania Univ., Philadelphia)
Met. Trans. 5, No. 2, 363-370 (February 1974)

A sample plate of HY 130 steel (5 pct Ni-0.5 pct Cr-0.5 pct Mo-0.1 pct V-0.1 pct C) was found to be quite susceptible to temper embrittlement. Step-cooling produced a shift in transition temperature of 585°K (310°C). In the step-cooled condition the plane strain stress intensity threshold for crack growth in 0.1 N H_2SO_4 was about 22 $MNm^{-3/2}$ (20 ksi $\sqrt{in.}$) and the fracture mode was intergranular, whereas in the unembrittled condition the threshold for a 1.27 cm (½ in.) plate (not fully plane strain) was around 104.5 $MNm^{-3/2}$ (95 ksi $\sqrt{in.}$) and the fracture mode was mixed cleavage and microvoid coalescence. The interaction between the impurity-induced and the hydrogen embrittlement is discussed in terms of Oriani's theory of hydrogen embrittlement.

Important References:

1. Anon., Electron Fractography Handbook, Supplement II, AFML-TR-64-416 (March 1968).

2. Cabral, U. Q., Hache, A., and Constant, A., Determination of Annealing Brittleness by Corrosion Tests under Tension in the Presence of Hydrogen, C. R. Acad. Sci. (Paris) 260, No. 26, 6887-6890 (June 28, 1965).

Key words: Crack propagation; ductile-brittle transition; high strength steels; hydrogen embrittlement; notched specimens; pre-cracked specimens; plates (structural); temper embrittlement; theories.

THE ROLE OF SURFACE STRESS ON HYDROGEN ABSORPTION BY 4340 STEEL
Phalen, D. I. and Vaughan, D. A. (Battelle Columbus Labs., OH)
Corrosion 24, No. 8, 243-246 (August 1968).

The reaction kinetics of stressed, high strength steel with cathodically generated hydrogen are shown to follow the first-order rate equation, with rate constant $K = 0.5 \times 10^5 \exp(-9700/RT)$ in which the activation energy is equivalent to that for diffusion of hydrogen in iron. The pre-exponential constant, however, is several orders of magnitude greater than that obtained for diffusion and is discussed in terms of the number of reactive sites. While the number of incipient sites is believed to be comparable to the number of subgrain (domain) boundaries in martensite (10^{12} cm^{-2}), a stress of 85 ksi activates approximately 10^7 sites/cm^2. These sites are not activated by a surface tensile stress of less than 40 to 50 ksi. When these sites are activated, however, hydrogen diffuses the area of higher tensile stress. In the case of ferritic structure, the hydrogen reaction rate does not increase with the magnitude of the tensile stress.

Important References:

1. Elsea, A. R. and Fletcher, E. E., Hydrogen-Induced, Delayed Brittle Failures of High Strength Steels, DMIC Report 196 (January 1964).

2. Smialowski, M., Hydrogen in Steel, Pergamon Press Ltd., London (1962).

3. Vaughan, D. A. and Phalen, D. I., The Effect of Hydrogen on the Structural Properties of Stainless Steel as Related to Its Corrosive Behavior, Metals Eng. Quart. 5, No. 3, 39-43 (August 1965).

4. Vaughan, D. A. and Phalen, D. I., Reactions Contributing to the Formation of Susceptible Paths for Stress Corrosion Cracking, in ASTM STP-425, 209-227 (1967).

Key words: Absorption; diffusion; embrittlement; failures (materials); high strength steels; hydrogen; martensite; tensile stress.

HYDROGEN PERMEABILITY AND DELAYED FAILURE OF POLARIZED MARTENSITIC STEELS
Barth, C. F., Steigerwald, E. A., and Troiano, A. R. (TRW Equipment Labs., Cleveland, OH.; Case Western Reserve Univ., Cleveland, OH)
Corrosion 25, No. 9, 353-358 (September 1969).

Hydrogen permeability and delayed failure characteristics were directly correlated under cathodic and anodic polarization for 9-4-45 and 4340 high strength steels. At cathodic potentials they both exhibited the usual increased susceptibility to failure with increasing cathodic potential. With increasingly anodic applied potential, the 9-4-45 displayed decreased times to failure, increased hydrogen permeability and surface pitting. The time to failure in 4340 did not respond to anodic polarization; there was no hydrogen permeation and no pitting. The concept of a generalized hydrogen embrittlement mechanism for stress corrosion cracking becomes increasingly attractive, since it is apparent that increased susceptibility to delayed failure under anodic potentials does not, per se, rule out the availability of hydrogen.

Important References:

1. Hancock, G. G. and Johnson, H. H., Hydrogen, Oxygen, and Subcritical Crack Growth in a High-Strength Steel, Trans. AIME 236, 513 (April 1966).

2. Troiano, A. R. and Whiteman, M. B., Hydrogen Embrittlement of Austenitic Stainless Steel, Corrosion 21, 53 (1965).

3. Phelps, E. H. and Loginow, A. W., Stress Corrosion of Steels for Aircraft and Missiles, Corrosion 16, 325T (July 1969).

4. Hughes, P. C., Lamborn, I. R., and Licbert, B. B., Delayed Fracture of a Low-Alloy High-Strength Steel at Controlled Corrosion Rates, J. Iron and Steel Ind., 728-731 (July 1965).

5. Shively, J. H., Hehemann, R. F., and Troiano, A. R., Hydrogen Permeability in a Stable Austenitic Stainless Steel under Anodic Polarization, Corrosion 23, 215 (1967).

6. Benjamin, W. D. and Steigerwald, E. A., Stress Corrosion Cracking Mechanisms in Martensitic High Strength Steel, AFML-TR-67-98 (1967).

Key words: Anodic polarization; cathodic polarization; embrittlement; failures (materials); high strength steels; hydrogen; martensite; material degradation; permeability; stress corrosion cracking.

A NEW MODEL FOR HYDROGEN-ASSISTED CRACKING (HYDROGEN EMBRITTLEMENT)
Beachem, C. D. (Naval Research Lab., Washington DC)
Met. Trans. 3, 437-451 (February 1972).

A new model is presented for hydrogen-assisted cracking (HAC) which explains the observations of decreasing microscopic plasticity and changes of fracture modes with decreasing stress intensities and crack tips during stress corrosion cracking and HAC of quenched and tempered steels. The model suggests that the presence of sufficiently concentrated hydrogen dissolved in the lattice just ahead of the crack tip aids whatever deformation processes the microstructure will allow. Intergranular quasicleavage, or microvoid coalescence fracture modes operate depending upon the microstructure, the crack-tip stress intensity, and the concentration of hydrogen. The basic hydrogen-steel interaction appears to be an easing of dislocation motion or generation, or both.

Important References:

1. Smith, J. A., Peterson, M. H., and Brown, B. F., Electrochemical Conditions at the Tip of an Advancing Stress Corrosion Crack in AISI 4340 Steel, Corrosion 26, No. 12, 539-542 (December 1970).

2. Westlake, D. G., A Generalized Model for Hydrogen Embrittlement, Trans. ASM 62, No. 4, 1000-1006 (1969).

3. Barth, C. F. and Steigerwald, E. A., Evaluation of Hydrogen Embrittlement Mechanisms, Met. Trans. 1, 3451-3455 (December 1970).

Key words: Brittle fracture; cracking (fracturing); deformation; diffusion; embrittlement; failure mechanisms; failure modes; fractures (materials); hydrogen; microstructure; models; stress corrosion; theories.

HYDROGEN MOVEMENT IN STEEL - ENTRY, DIFFUSION, AND ELIMINATION
Fletcher, E. E. and Elsea, A. R. (Battelle Memorial Inst., Columbus, OH)
DMIC Report 219 (June 1965).

This report was prepared to aid in understanding the movement of hydrogen in steel. It considers ways in which hydrogen enters steels, how it moves through steel, and methods whereby it may be removed from steel. The various factors that affect each of these phenomena are considered. The first section of the report deals with the solubility of hydrogen, and such aspects of solubility as preferred lattice sites for hydrogen, lattice expansion, measurements of solubility, and estimates of equilibrium hydrogen pressure in steel are discussed. The second section concerns the permeating of hydrogen through steel. Factors which influence the rate of hydrogen removal from iron and steel, such as temperature, section size, external environment, and coatings on the steel, are dealt with in the final section of the report.

(FOR LISTING OF IMPORTANT REFERENCES, KEYWORDS AND A DUPLICATE ABSTRACT, SEE PAGE 63).

CONTROL AND APPLICATION OF ENVIRONMENT SENSITIVE FRACTURE PROCESSES
Westwood, A. R. C. (Martin Marietta Labs., Baltimore, MD)
In Proc. Tewksbury, Symp. Fracture, Effects of Chemical Environments on Fracture Processes, Melbourne, Univ., Australia (4-6 June 1974).

Chemically active environments can influence fracture processes in all types of solids, and our ability to minimize their usually detrimental influences on component reliability, and capitalize on their sometimes beneficial influences on materials removal processes, is likely to be directly related to our level of mechanistic or conceptual understanding of such effects. At present, such understanding is extremely limited. In part, this is a consequence of our inadequate comprehension of some of the fundamental processes involved, e.g., of the specific electronic interactions which occur between adsorbates and absorbents during chemisorption, and of the influence, if any, of lattice strain on such interactions. Perhaps the greater obstacle to immediate progress, however, is the interdisciplinary nature of this field of study, involving as it does the complicated interplay of variables arising from the chemistry of the environment, the physics of the near-surface layers of the solid, and the materials science and engineering of the bulk. In the paper phenomena such as stress corrosion cracking, liquid metal embrittlement and chemo-mechanical effects are considered as they relate to the fracture behavior of metals, ceramics, minerals, rocks, glasses, organic crystals and polymers.

Comment:

The author has presented a detailed tutorial paper in which he effectively argues for a more interdisciplinary approach to the study of the interaction between a metal and its environment. His presentation of the basic chemistry and physics of the process is a good reminder that the empirical and mechanical approaches must be tempered by the understanding of the basic nature of the mechanisms. In particular, his postulations on the long range effects on fracture processes of the electronic interactions between adsorbates and absorbents should receive further study.

Important References:

1. Preece, C. M. and Westwood, A. R. C., Temperature-Sensitive Embrittlement of FCC Metals by Liquid Metal Solutions, Trans. ASM 62, No. 2, 418-425 (1969).

2. Floreen, S., Hayden, H. W., and Kenyon, N., Stress Corrosion Cracking Behavior of Maraging Steel Composites, Corrosion 27, 519-524 (1971).

3. Sedricks, A. J. and Green, J. A. S., Stress Corrosion of Titanium in Organic Liquids, J. Metals 23, 48-54 (1971).

4. Latanision, R. M., and Staehle, R. W., Plastic Deformation of Electrochemically Polarized Nickel Single Crystals, Acta Met. 17, No. 3, 307-319 (1969).

5. Wicks, B. J. and Lewis, M. H., The Effect of Impurities on the Flaw Stress of Magnesium Oxide Single Crystals, Phys. Stat. Solidi. 6, No. 1, 281-294 (1971).

6. Westwood, A. R. C. and Goldheim, D. L., Mechanism for Environmental Control of Drilling in MgO and CaF_2 Monocrystals, J. Amer. Ceram. Soc. 53, No. 3, 142-147 (1970).

Key words: Ceramics; chemical reactions; corrosion; cracking (fracturing); environment effects; fracture mechanics; gas embrittlement; grain boundaries; hydrogen; material defects; microstructure; models; surface cracks; theories.

V - APPLICATION/SERVICE EXPERIENCE

FACTORS AFFECTING THE SULFIDE STRESS CRACKING PERFORMANCE OF HIGH STRENGTH STEELS
Greer, J. B. (Esso Production Research Co., Houston, TX)
Mater. Perform., 11-22 (March 1975).

Environmental, metallurgical, and stress effects on high strength steel performance in sour environments are summarized. Environmental variables with respect to manufacture and design of tubular goods for deep, sour wells are interpreted. A large number of illustrations are used to present time-to-failure data, hydrogen penetration rate as a function of H_2S concentration, temperature effects, fatigue curves, etc. There are 51 references.

Comment:

The author has presented a wealth of empirical information on the sulfide stress cracking problem. It is of interest to note that the high strength steels considered in this paper are in the 125 to 150 thousand psi range. This paper highlights the empirical approach that the industry has been forced to employ in attacking this problem. This illustrates the necessity for theoretical work in this area and the transfer of this to the practical sphere.

Important References:

1. Phelps, F. H., A Review of the Stress Corrosion Behavior of Steels with High Yield Strength, Proc. Conf. Fundamental Aspects of Stress Corrosion Cracking, NACE (1969).

2. Hudgins, C. M., The Effect of Temperature on the Aqueous Sulfide Stress Cracking Behavior of an N-80 Steel, NACE Canadian Western Regional Conf. (1971).

3. Lasater, R. M., Kenney, B. R., and Knox, J. A., Prevention of Hydrogen Sulfide Cracking of High Strength Carbon Steels in Acid Systems, NACE Annu. Conf. 23rd (1967).

4. Judy, Jr., R. W. and Goode, R. J., Procedure for Stress Corrosion Cracking Characterization and Interpretation to Failure-Safe Design for High Strength Steels, Proc. NACE Annu. Conf., 26th (1970).

5. Novak, S. R. and Rolfe, S. T., Comparison of Fracture Mechanics and Nominal-Stress Analyses in Stress Corrosion Testing (Proc. 26th Annual Conf. NACE (1970).

6. Bucci, R. J., Paris, P. C., Loushin, L. L., and Johnson, H. H., A Fracture Mechanics Consideration of Hydrogen Sulfide Cracking in High Strength Steels, ASTM STP-513, Part 1, 292-307 (September 1972).

Key words: Brittle fractures; corrosion; environmental effects; high strength steels; microstructures; stress corrosion cracking; sulfide stress cracking; temperature effects.

STRESS-CORROSION AND HYDROGEN-EMBRITTLEMENT BEHAVIOR OF LINE-PIPE STEEL IN UNDERGROUND ENVIRONMENTS
Vrable, J. B. (West Virginia, Univ., Morgantown, WV)
W. Va. Univ., Eng. Exp. Sta., Tech. Bull. No. 106, 299-310 (1972).

Over the years, stress-corrosion cracking has been encountered in carbon steels and low-alloy steels in only a very limited number of corrosive environments. The most common of these are hot and concentrated nitrate environments, hot caustic solutions, contaminated anhydrous ammonia, and, for higher strength steels, sulfide environments. In the recent past, however, there have been several failures of gas-transmission pipelines that have been attributed to stress-corrosion cracking under soil exposure conditions which do not correspond with any of the previous environments known to cause these phenomena. Moreover, cracking-type failures initiating in "hard spots" have been attributed to hydrogen embrittlement. As a result of these reports, a substantial interest has developed in establishing valid methods for detecting and recognizing stress-corrosion cracking and hydrogen embrittlement in line-pipe steels. The characteristics of both of these types of cracking are described. In addition, several examples of pipeline cracking are cited with emphasis on the investigative work performed to establish the cause and the nature of these cracks. Current thinking with respect to avoiding stress corrosion and hydrogen embrittlement in future installations is also described.

(FOR LISTING OF IMPORTANT REFERENCES, KEYWORDS AND A DUPLICATE ABSTRACT, SEE PAGE 59).

SULFIDATION PROPERTIES OF NICKEL - 20WT. % MOLYBDENUM ALLOY IN HYDROGEN-HYDROGEN SULFIDE ATMOSPHERES AT 700°C
Young, D. J., Smeltzer, W. W., and Kirkaldy, J. S. (Hamilton Univ., Ontario, Canada)
Oxid. Metals 7, No. 3, 149-161 (1973).

The sulphidation kinetics and morphological development of the reaction products for a Ni-20 wt. % Mo alloy exposed at 700°C to hydrogen and hydrogen sulfide atm at sulfur pressures in the range 1×10^{-11} to 2×10^{-2} atm are reported. At less than 5×10^{-11} atm, the reaction product was molybdenum sulfide which grew as an external scale by parabolic kinetics. For pressures between 1×10^{-10} and 4×10^{-10} atm, the simultaneous internal precipitation and external growth of molybdenum sulfide occurred by linear kinetics. An external duplex scale was formed at sulfur pressures between 2×10^{-8} to 2×10^{-2} atm in which the inner layer was a two-phase mixture of molybdenum sulfide and nickel sulfide, and the outer layer contained solid nickel sulfides and a liquid Ni-Mo sulfide phase. Catastrophic linear kinetics occurred under the latter conditions.

Important References:

1. Strafford, K. N. and Hampton, A. F., Sulphidation of Chromium and Some Chromium-Molybdenum Alloys; Kinetic and Morphological Features of the Process, J. Less-Comm. Met. 21, No. 3, 305-324 (July 1970).

2. Gerlach, Jr., and Hamel, H. J., High Temperature Sulfidation of Tungsten and Molybdenum in H_2/H_2S Mixtures and in Sulfur Vapor, Metall. 24, No. 5, 488-494 (May 1970).

3. Young, D. J., Smeltzer, W. W., and Kirkaldy, J. S., Nonstoichiometry and Thermodynamics of Chromium Sulfides, J. Electrochem. Soc. 120, No. 9, 1221-1224 (September 1973).

4. Chitty, J. A. and Smeltzer, W. S., Sulfidation Properties of a Nickel - 20 w/o Chromium Alloy at 700°C and Low Sulfur Pressures, J. Electrochem. Soc. 120, No. 10, 1362-1368 (October 1973).

Key words: Chemical reactions; corrosion; hot corrosion; hydrogen; molybdenum alloys; nickel alloys.

HYDROGEN STRESS CRACKING OF A REFORMER REACTOR
Reid, L. H. (Sun Oil Co., Marcus Hook, PA)
In Proc. Amer. Petrol. Inst., Sec. III. Refining 53, 431-436 (1973).

The report is a description of the failure of a large reformer reactor vessel. Cracks developed in the fillet weld joining the nozzle reinforcing pads to the head, and in the nozzle forging. Fractographic evidence indicated that the cracks started from hot spots in the nozzle forging and weldment and from hard fillet welds in the same area. Metallographic evidence indicated that the cracks and fissures resulted from hydrogen stress cracking.

Important References:

1. Anon., Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants, API Pub. No. 941 (1970).

2. Groenveld, T. P. and Elsea, A. R., Effect of Hydrogen in the Properties of Reactor Steels Below 400°F, Battelle Columbus Lab. (December 1971).

3. Nelson, G. A., Interpretive Report on Effect of Hydrogen in Pressure Vessel Steels, WRC Bull. No. 145, 38 (1969).

Key words: Corrosion; cracking (fracturing); failures (materials); hydrogen; pressure vessels; stress corrosion cracking; stress rupture; welded structures.

SULFIDE STRESS CORROSION CRACKING OF STEELS
Dvoracek, L. M. (Union Oil Co. of California, Brea.)
Corrosion 26, No. 5, 177-188 (May 1970).

Critical nominal stress and critical stress intensity factors for sulfide stress corrosion cracking of various steels were determined using fatigue-precracked, laboratory, cantilever beam specimens and short lengths of oil field casing and tubing pressured to failure. The laboratory critical constants were found to be lower than those obtained from short lengths of casing and tubing containing longitudinal internal surface notches. Acceptable steels were defined by statistical methods as those which did not crack in sulfide environments when stressed to their yield strength. The effects of sodium chloride, pH, hydrogen sulfide concentration, temperature, cold working, heat treatment and strength of the steel on these critical constants were determined. Critical flaw sizes which can be used for inspection were calculated from the critical stress intensity factors.

Important References:

1. Treseder, R. S. and Swanson, T. M., Factors in Sulfide Corrosion Cracking of High Strength Steels, Corrosion 24, No. 2, 31-37 (February 1968).

2. Snape, E., Roles of Composition and Microstructure in Sulfide Cracking of Steel, Corrosion 24, No. 9, 261-282 (September 1968).

3. Snape, E., Schaller, F. W., and Forbes, R. M., A Method for Improving Sulfide Cracking Resistance of Low Alloy Steels, Corrosion 25, No. 9, 380 (September 1969).

4. Snape, E., Sulfide Stress Corrosion of Some Medium and Low Alloy Steels, Corrosion 23, No. 6, 154-172 (June 1967).

5. Elsea, A. R. and Fletcher, E. E., Hydrogen Induced, Delayed, Brittle Failures of High Strength Steel, DMIC Report 196 (January 1964).

6. Fletcher, E. E. and Elsea, A. R., Hydrogen Movement in Steel - Entry, Diffusion, and Elimination, DMIC Report 219 (June 1965).

Key words: Cracking (fracturing); fatigue (materials); fracture strength; pipes (tubes); stress corrosion; stress corrosion cracking; stress intensity factor.

HYDROGEN PENETRATION AND DAMAGE TO OIL FIELD STEELS
Martin, R. L. (Pretrolite Corp., St. Louis, MO)
Mater. Perform. 13, No. 7, 19-23 (July 1974)

A systematic look has been taken at the hydrogen embrittlement aspect of cracking failures in oil field steels. Using two laboratory methods, one a simple U-bend stress cracking test and the other a hollow tube hydrogen permeation probe, the effect of such variables as H_2S to CO_2 ratio, chloride concentration, hydrocarbon, suspended corrosion products, and corrosion inhibitors on general corrosion and hydrogen permeation is examined. Possible explanations are offered for the above observations in terms of the surface corrosion product layer. Relevance of these observations to cracking failures in oil field equipment is discussed. The conclusions presented by the author are: (1) Hydrogen penetration and associated steel damage caused by corrosion in H_2S-laden fluids can be greatly reduced by selected organic corrosion inhibitors; (2) This principal has been demonstrated in drilling fluids contaminated with sour gas in field situations; (3) The amount of hydrogen penetrating corroding steel in sour fluids depends first on the total amount generated by the corrosion; and second, probably depends on the conductivity characteristics of the corrosion product layer, which in turn could dictate the depth of hydrogen ion cathodic discharge in the layer; and (4) The presence of hydrocarbon in a sour corrodent system lowers hydrogen entry into steel in both inhibited and uninhibited systems.

Important References:

1. Snape, E., Roles of Composition and Microstructure in Sulfide Cracking of Steel, Corrosion 24, No. 9, 261-282 (September 1968).

2. Dvoracek, L. M., Sulfide Stress Corrosion Cracking of Steels, Corrosion 26, No. 5, 177-188 (May 1970).

3. Tresader, R. S. and Swanson, T. M., Factors in Sulfide Corrosion Cracking of High Strength Steels, Corrosion 24, No. 2, 31-37 (February 1968).

4. Smialowski, M. Hydrogen in Steel, Pergamon Press Ltd., London (1962).

5. Snape, E., Schaller, F. W., and Forbes, R. M., A Method for Improving Sulfide Cracking Resistance of Low Alloy Steels, Corrosion 25, No. 9, 380 (September 1969).

6. Hudgins, C. M. and McGlasson, R. L., The Effects of Temperature (70-400°F) on the Aqueous Sulfide Stress Cracking of an N-80 Type Steel, Paper presented at NACE Canadian Western Regional Conf. (February 1971).

7. Dieter, Jr., G. E., Mechanical Metallurgy, McGraw-Hill, New York, NY (1961).

8. Nathan, C. C., Dulaney, C. L., and Leary, M. J., Localized Corrosion - Cause of Metal Failure, in ASTM STP-516 (1972).

9. Annand, R. R. and Martin, R. L., A New Inhibitor for Corrosion in Aerated Sour Waters, Paper presented at AIME, Oil Field Water Handling Conf., Los Angeles, CA (December 1972).

10. Barth, C. F. and Troiano, A. R., Cathodic Protection and Hydrogen in Stress Corrosion Cracking, Corrosion 28, No. 7, 259-263 (July 1972).

Key words: Corrosion; cracking (fracturing); embrittlement; fatigue (materials); hydrogen; pipes (tubes); steels; structural alloys; tensile strength; yield strength.

STRESS CORROSION CRACKING AND HYDROGEN EMBRITTLEMENT OF HIGH-STRENGTH FASTENERS
Stanley, J. K. (Aerospace Corp., El Segundo, CA)
J. Spacecr. Rockets 9, No. 11, 796-804 (November 1972).

Unexplained brittle failures of high strength fasteners on aerospace vehicles have been caused by stress corrosion cracking (SCC) and by hydrogen stress cracking (HSC). Confusion exists as to the nature of each phenomenon. The poorly understood failure mechanisms are difficult to differentiate, especially in the field. There is a growing acceptance of the term SCC to cover failures by both mechanisms. Data are given to characterize the classes. For low alloy carbon steels, heat treated to yield strengths below approximately 160 ksi, stress corrosion is not a problem, nor is hydrogen embrittlement (delayed cracking) very common. Above this, stress difficulties can occur. The high strength precipitation hardening stainless steels have varying degrees of resistance to SCC and hydrogen embrittlement, depending upon the strength level and heat treating procedures that influence the microstructure. Use of plane strain fracture toughness K_{IC} and the stress corrosion threshold of K_{ISCC} offers promise of selecting optimum bolting for a specific environment. The attractiveness of K_{IC} analysis is that it does not differentiate between failure mechanisms; failure can be due to either SCC or HSC.

Important References:

1. Stanley, J. K., Solutions to Some Stress Corrosion Cracking Problems in Aerospace Situations, Proc. Joint Aerospace and Marine Corrosion Technol. Seminar, 1st, Houston, TX (1969).

2. Lucas, W. R., Report of the Ad Hoc Committee on Failure of High Strength Materials, NASA Marshall Space Flight Center, Huntsville, AL (1971).

3. Dull, D. L. and Raymond, L., A Method of Evaluating Relative Susceptibility of Bolting Material to Stress Corrosion Cracking, Paper presented at WESTEC Conf., (March 1972).

4. LeGrand, J. and Conderc, C., A Fractographic Study of Hydrogen Gas Embrittlement in Steels, Trans. AIME (1972).

5. Freedman, A. J., Development of an Accelerated Stress Corrosion Test for Ferrous and Nickel Alloys, Northrop Corp., Report NOR-68-58 (April 1968).

Key words: Brittle fractures; cracking (fracturing); failures (materials); hydrogen embrittlement; material degradation; stress corrosion cracking.

EXPLORATORY DEVELOPMENT ON HYDROGEN EMBRITTLEMENT OF HIGH STRENGTH STEEL DURING MACHINING

Das, K. B. (Boeing Co., Seattle, WS)

AFML-TR-73-244 (1973).

The possibility of machining fluid being a source of hydrogen during the fabrication process was investigated. Failure of high strength steel structures can occur as a result of hydrogen embrittlement due to absorption during fabrication or when the hardware is in use. Test specimens made of 4340 steel (heat treated to 260 psi - 280 psi strength level) of known hydrogen concentration were subjected to a specified schedule of gentle and abusive milling and grinding operations using different machining fluids. Following the machining operations the specimens were analyzed for excess hydrogen above the base level with a Boeing developed ultrasensitive hydrogen analysis system. A total of six different machining fluids with different active chemical components were used. Experimental results are presented with a statistical analysis of the hydrogen concentration data.

(FOR LISTING OF IMPORTANT REFERENCES, KEYWORDS AND A DUPLICATE ABSTRACT, SEE PAGE 64).

HYDROGEN EMBRITTLEMENT OF 4340 STEEL AS A RESULT OF CORROSION OF POROUS ELECTROPLATED CADMIUM
Rinker, J. G. and Hochman, R. F. (Georgia Inst. of Tech., Atlanta)
Corrosion 28, No. 6, 231-232 (June 1972).

Delayed failure of AISI 4340 steel with a low hydrogen embrittlement cadmium plating was studied in air and in an aqueous solution of 3.5 percent sodium chloride. Due to the cadmium steel couple which exists in the salt solution, the change in plating porosity appears to increase the amount of cathode area (exposed steel). The shorter times to failure for the baked (more porous) specimens may be accounted for by the observed effects of the baking treatment on the cadmium electrodeposit.

Important References:

1. Peterson, M. H., Brown, B. F., Newbegin, R. L. and Groover, R. E., Stress Corrosion Cracking of High Strength Steels and Titanium Alloys in Chloride Solutions at Ambient Temperature, Corrosion 23, No. 5, 142-148, (May 1967).

Key words: Corrosion; delayed failure; failure mechanisms; fracture mechanics; hydrogen embrittlement; metallography.

SURVEY OF HYDROGEN COMPATIBILITY PROBLEMS IN ENERGY TRANSMISSION APPLICATIONS
Swisher, J. H., Keeton, S. C., West, A. J., and Jones, A. T. (Sandia Corp., Albuquerque, NM; Sandia Corp., Livermore, CA)
Sandia Report SAND74-8219 (September 1974).

A study has been made of current energy storage and transmission applications in which containment of hydrogen is a consideration. The applications discussed are hydrogen storage in hydrides, pressure vessels and pipelines for hydrogen, superconducting electrical transmission lines, and superconducting magnets for storing magnetic energy. The most difficult problems of those discussed are in the design and construction of pressure vessels and pipelines for high pressure hydrogen, because of the size of the facilities, quality control is difficult and low-cost materials must be used. In underground pipelines, the problems are compounded by possible corrosive attack leading to crack formation. In hydride storage and cryogenic application, the principal need for materials work is in performance - cost tradeoff studies between stainless steels and lower cost substitutes. Even if stainless steels are used, some potential problems exist and qualification tests should be conducted.

Important References:

1. Strickland, G., Reilly, J. J. and Wiswall, R. H., in Proc. of the Hydrogen Economy Miami Energy Conf., Miami Univ. (March 1974).

Key words: Crack analysis; crack formation; design criteria; fracture strength; gas embrittlement; hydrogen; material defects; safety criteria; stainless steels; stress intensity factor.

AUTHOR INDEX

This Index lists the name of each author, or co-author of a document that is abstracted in this report and also the names of the authors or co-authors of all important references cited with the abstracts. Authors of documents that are abstracted are identified by an asterisk (*).

KEY WORD INDEX