INFORMATION TO USERS

The most advanced technology has been used to photograph and reproduce this manuscript from the microfilm master. UMI films the original text directly from the copy submitted. Thus, some dissertation copies are in typewriter face, while others may be from a computer printer.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyrighted material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each oversize page is available as one exposure on a standard 35 mm slide or as a $17'' \times 23''$ black and white photographic print for an additional charge.

Photographs included in the original manuscript have been reproduced xerographically in this copy. 35 mm slides or $6'' \times 9''$ black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

Order Number 8803207

Mechanics of hydrogen embrittlement

Sofronis, Petros, Ph.D.

University of Illinois at Urbana-Champaign, 1987

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

PLEASE NOTE:

In all cases this material has been filmed in the best possible way from the available copy.
Problems encountered with this document have been identified here with a check mark __✓__ .

1. Glossy photographs or pages _____

2. Colored illustrations, paper or print _____

3. Photographs with dark background _____

4. Illustrations are poor copy _____

5. Pages with black marks, not original copy _____

6. Print shows through as there is text on both sides of page _____

7. Indistinct, broken or small print on several pages __✓__

8. Print exceeds margin requirements _____

9. Tightly bound copy with print lost in spine _____

10. Computer printout pages with indistinct print _____

11. Page(s) _____ lacking when material received, and not available from school or author.

12. Page(s) _____ seem to be missing in numbering only as text follows.

13. Two pages numbered _____ . Text follows.

14. Curling and wrinkled pages _____

15. Dissertation contains pages with print at a slant, filmed as received _____

16. Other_____

_____

_____

U·M·I

MECHANICS OF HYDROGEN EMBRITTLEMENT

BY

PETROS SOFRONIS

Dipl., Aristoteleion University of Thessaloniki, 1980
M.S., University of Illinois, 1983

THESIS

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Theoretical and Applied Mechanics
in the Graduate College of the
University of Illinois at Urbana-Champaign, 1987

Urbana, Illinois

UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

THE GRADUATE COLLEGE

JUNE 1987

WE HEREBY RECOMMEND THAT THE THESIS BY

PETROS SOFRONIS

ENTITLED   MECHANICS OF HYDROGEN EMBRITTLEMENT

BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR

THE DEGREE OF   DOCTOR OF PHILOSOPHY

R. M. McMeeking

Director of Thesis Research

Head of Department

Committee on Final Examination†

R. M. McMeeking

Chairperson

† Required for doctor's degree but not for master's.

O-517

To my parents,

Anna and Athanasios,

antidôron

ACKNOWLEDGMENT

I would like to express my deepest appreciation to my advisor, Professor Robert M. McMeeking, for having shown and taught me how to conduct research "on my own." In addition, I would like to thank him for his scientific guidance, support and encouragement, especially during the difficult times of this work. I ought not to forget to mention our friendly and enriching discussions, such as those on the constitutional history of Britain.

I also owe a special thanks to Professor Howard K. Birnbaum for his elucidating explanations of several physical aspects of hydrogen embrittlement, and to Professor Anthony G. Evans for his valuable observations during the development of this work.

In the course of this work friendship reemerged as the most significant bond in my life. My friends Nikos Aravas and Aspa Zerva, George and Annita Skarpathiotis, Thomas Stoicos and Nike Skarlatos, Christos and Tonia Nikolaides, Nikos Andritsos, Stefanos Sakellarides and Apostolos Athanasakis have made life joyful, while Kyriakos Petropoulos and Titika Mylopoulou, Anestis and Pelagia Diamandides, Sakis Pyredjides, Demetris Menexides, George Fanaropoulos and Nikos Tseflios have proved that it is special people that make the difference.

Not of less importance were the discussions on thermodynamics with my friend James Lund during summer of 1986, and those while jogging along the Isla Vista Beach. My heartfelt thanks also go to Allan Grapard for his friendship and illuminating views on Western European thought.

Lastly, I would like to express my profound appreciation to my steadfast friend, Miss Lenna Petropoulou. Her support was unflagging, and her patience and devotion shall remain indelible in my memory.

TABLE OF CONTENTS

Page

CHAPTER 1

General Overview of Hydrogen Embrittlement

1.1 Introduction

In this chapter the hydrogen embrittlement phenomenon is outlined and hydrogen degradation effects on the materials are described. The literature is reviewed from a fracture mechanics standpoint, and finally the basic features and objectives of our method of analysis are presented.

1.2 Hydrogen Embrittlement

Hydrogen is a deleterious solute impurity in pure metals and alloys known to be detrimental to almost all systems as regards their fracture behavior. Its degrading effect on the mechanical properties of materials has been extensively analyzed and the related literature is voluminous. Several researchers have provided informative overviews (Birnbaum [1]*, [2], [3]; Hirth [4], [5]; Latanision [6]; Johnson [7]). The damaging hydrogen effect is reported generally under the term "hydrogen embrittlement" and is a phenomenon not completely understood despite the intense investigation it has received.

According to Nelson [8] and Johnson [9] hydrogen embrittlement may be defined as a material degradation caused by the presence of hydrogen under load. It manifests itself on various parameters that are used as measures

---

*Numbers in brackets indicate the references quoted at the end of the text.

of the mechanical properties of materials such as elongation to failure, reduction of area, strain hardening rate, tensile strength, fracture toughness, and time to failure. As a consequence, the degraded materials often fail prematurely and sometimes catastrophically (McPherson [10], Waisman et al. [11]). The severity of the degradation is influenced by the microstructure (Thompson and Bernstein [12]) and appears to be controlled by various combinations of metallurgical variables such as chemical composition, grain size, texture and thermal treatment (Bernstein and Thompson [13]). Also, operating conditions such as hydrogen fugacity, temperature and strain rate have been determined to play a role in the degree of susceptibility and the characteristics of fractures (Birnbaum [3]; Dutton [14]).

It must be emphasized that the term embrittlement refers generally to the macroscopically measured ductility, strength and toughness parameters. Thompson and Bernstein [15] point out that changes in macroscopic ductility, strength or toughness need not and often do not result from failures which involve cleavage.

Categorizing hydrogen embrittlement, one may distinguish embrittled systems into two broad classes. The first one includes the hydride forming systems. In these systems, hydrogen reacts chemically with the metals forming hydrides. The second one, where no such reaction occurs, includes the non-hydride forming systems. In order to describe the two categories the concept of heat of solution is introduced. It is a measure of the ability of metals to dissolve hydrogen (Lee [16]; Westlake [17]) and expresses the difference in energy of a hydrogen atom dissolved in the

metal and in the form of a hydrogen gas molecule under constant pressure (Piercy [18]; Fast [19]; Speiser [20]).

The hydride forming systems are those which have thermodynamically stable hydrides and those whose hydrides are stabilized by deformation (Birnbaum [2]). Representative of those systems are the metals niobium, zirconium, titanium, vanadium and their alloys. They are also called exothermic occluders because the heat of solution is negative. Hence, the hydrogen solubility decreases with increasing temperature. Representative non-hydride forming systems are iron, nickel, aluminum and their alloys. They are also called endothermic occluders because the heat of solution is positive. Consequently, the hydrogen solubility increases with increasing temperature. In the next section, hydrogen embrittlement effects are reported as observed in practice.

1.3 Description of the Hydrogen Degradation Phenomena

Hydrogen is present in the materials internally as solid solute, externally as gaseous H_2, as a dissociated molecule, or as a complex molecule such as a hydrogen sulfide, water or methane (Nelson [8]). Even though the phenomenology and kinetics of fracture are affected by the source of hydrogen (Birnbaum [3]; Johnson [9]; Nelson [8]), it appears that for a given alloy there are no inherent differences in the mechanisms causing degradation (Gerberich et al. [21]; Viswanathan and Hudak [22]; Oriani [23]). Furthermore, experimental evidence suggests that the metal-hydrogen interactions are the very basis of the hydrogen embrittlement mechanisms (Nelson [8]). Indeed, it has been established that the inter-

action of hydrogen with the lattice and defects in the vicinity of a major macrocrack is the common factor of all degradation phenomena (Smialowski [24]). Keeping this in mind, we shall classify phenomenologically the hydrogen degradations into the following categories (Hirth and Johnson [25]; Dutton [14]):

i) <u>Hydrogen Stress Cracking</u>: Also known as hydrogen induced delayed brittle failure or internal hydrogen embrittlement. Hydrogen exists as an internal solute. Ductile steels fail this way under sustained loads causing nominal stresses below the yield stress. In other words, the material was capable of safely bearing the load in the absence of hydrogen. This type of failure is particularly insidious because there exists an incubation period before the unexpected fracture. The higher the tensile strength of the material the lower the levels of loadings capable of causing fractures.

ii) <u>Hydrogen Environmental Embrittlement</u>: It occurs in materials such as ferritic and austenitic steels and nickel alloys which undergo deformation in the presence of gaseous hydrogen. Strain rates, alloy purity and hydrogen fugacity are very important factors. High strength steels suffer this sort of degradation in a more pronounced manner.

iii) <u>Loss in Tensile Ductility</u>: An inability of all steels to accommodate macroscopic plastic deformation. The effect is sens .ve to strain rates and directly proportional to hydrogen content in solution.

iv) <u>Hydride Formation</u>: Under certain conditions of hydrogen content and stress, hydrides precipitate. Their extreme brittleness causes reduction of fracture toughness and delayed catastrophic failures have been

reported by Waisman et al. [11] in Zr-2.5 wt% Nb alloy and Simpson and Ells [26] in 6Al-4V-Ti alloy.

The degradation phenomena mentioned are those that are characterized by almost the same mechanisms as we have stated before. In addition, there are some others such as the blistering and hydrogen attack whose detailed descriptions are given by Hirth and Johnson [25].

So far, the types of hydrogen caused alloy degradations have been identified. In this work, attention is focused on analyzing the solute hydrogen effects as they result from the metal-hydrogen interactions. Phenomena related to the source of hydrogen and the kinetics of entry into the material are not considered. In particular, we are interested in types (i) and (ii) of the problems mentioned, in the sense that hydrogen enters the material, and then exists as a solid solute. The third case of problems (iii) is treated as a resulting feature of the general hydrogen embrittlement phenomenon and is assessed after the results of our analysis are obtained. Type (iv) problems are treated separately due to their distinct characteristics. In conclusion, the focus is concentrated mainly on the behavior of solute hydrogen. Under these conditions, the issue of hydrogen controlled degradations of the materials as it occurs in the hydride and non-hydride forming systems is addressed. Along these lines the literature is reviewed in the next section. The emphasis is put on works which mostly treat the phenomena from a fracture mechanics viewpoint. Other aspects such as metallurgical ones may be found in the overviews referenced in Section 1.2.

1.4 Review of Theories for Hydrogen Degradation

The complex characteristics of the subject have constituted a source of controversy. Our current understanding leads to the recognition that there is no single mechanism causing the hydrogen embrittlement. Rather it appears that different mechanisms apply to different systems under various conditions (Louthan and McNitt [27]).

In the non-hydride forming systems, first, Troiano [28] and his coworkers [29] made a systematic study of the hydrogen induced fractures. They concluded that the phenomenon is controlled by the diffusion of hydrogen into the crack tip region and is strongly influenced by the hydrostatic stress gradients. Analyzing crack growth kinetics, they postulated that a critical hydrogen concentration set up by the high stress triaxiality is necessary for the fracture phenomenon to initiate. This was justified by an incubation period they observed before the start of microcracking at sites well below the notch crack surfaces. Such brittle microcracking has also been reported later by Chu et al. [30] to be the cause of premature failures. However, the lack of advanced mechanics tools did not allow for definite assessments of the problem. Their work, though, forms the basis for subsequent investigations.

The decohesion concept was introduced by Steigerwald et al. [31] and Troiano [28] to explain these phenomena. It was further analyzed by Oriani [23] and studied on thermodynamic grounds by Hirth and Rice [32]. The model assumes that high hydrogen concentrations reduce the cohesive bonding force between the metal atoms. Hence, brittle fractures are the result of this cohesion reduction. The primary difficulty in validating

the mechanism is to relate the cohesive stress to a critical hydrogen concentration needed for decohesion. Also, experimentally observed ductile fractures do not favor full support for the mechanism. Based on the decohesion concept, models for crack initiation and subsequent crack growth kinetics were proposed by Oriani and Josephic [33], [34]; Gerberich et al. [21], [35] and Gerberich [36]. Oriani and Josephic [33], [34] found experimentally that the threshold stress intensity factor, K_H, for crack initiation was well below the fracture toughness K_c in the absence of hydrogen. They revealed that K_H decreases linearly with $\log(P_{H_2})$ where P_{H_2} is the pressure of the environmental hydrogen. Then, they related K_H to a critical hydrogen concentration as deduced from Sievert's law (Oriani [37]; Lee [16]) and qualified by the hydrostatic stress elevation (Li et al. [38]).

Gerberich et al. [21] used linear elastic fracture mechanics and the hydrostatic stress induced equilibrium concentration of hydrogen to predict relationships between external gaseous hydrogen pressure versus critical hydrogen concentration for crack propagation due to decohesion. Also, using basic plasticity ideas they related the critical hydrogen concentration to the threshold stress intensity factor K_H and found similarities with Oriani's and Josephic's results. Extending this work, Gerberich et al. [35] and Gerberich [36] studied crack growth kinetics, based again on linear analysis. More recently, Gerberich [39] considered hydrogen trapping at internal material defects in the region of high hydrostatic stress viewed as responsible for high hydrogen concentrations.

He located the hydrostatic stress elevation at a point in from the notch root. He also used a crack initiation criterion based on the effect on the decohesion stress that hydrogen may have. The mechanics he used was linear elastic, modified so as to account for plasticity.

Research on crack growth kinetics has also been carried out by other investigators such as Tien et al. [40] and Tien [41]. It has been well established that the crack growth rate follows a three stage pattern in mode I loading in a hydrogen atmosphere (Williams and Nelson [42]; Kerns and Staehle [43]). Fracture initiates at K_H and the crack velocity is strongly dependent on the applied stress intensity K_{app} (Stage I). At higher K_{app} (Stage II), crack velocity becomes almost independent of the stress intensity but strongly temperature dependent. When K_{app} reaches K_c (Stage III), unstable crack propagation begins which is independent of the hydrogen pressure.

Van Leeuwen [44], [45] described the stress assisted diffusion of hydrogen towards a crack tip. Based on the critical concentration concept for crack initiation he predicted incubation periods. However, he utilized linear elastic analysis. For instance, his diffusion equation does not contain the Laplacian of the hydrostatic stress since linear elastic material under plane strain conditions was assumed where such a quantity is zero. Similar linear elastic analysis at a crack tip was carried out by Liu [46]. Further work is necessary to determine which materials can be explained in terms of the decohesion model and when it operates.