INFORMATION TO USERS

While the most advanced technology has been used to photograph and reproduce this manuscript, the quality of the reproduction is heavily dependent upon the quality of the material submitted. For example:

- Manuscript pages may have indistinct print. In such cases, the best available copy has been filmed.
- Manuscripts may not always be complete. In such cases, a note will indicate that it is not possible to obtain missing pages.
- Copyrighted material may have been removed from the manuscript. In such cases, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, and charts) are photographed 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 also filmed as one exposure and is available, for an additional charge, as a standard 35mm slide or as a 17”x 23” black and white photographic print.

Most photographs reproduce acceptably on positive microfilm or microfiche but lack the clarity on xerographic copies made from the microfilm. For an additional charge, 35mm slides of 6”x 9” black and white photographic prints are available for any photographs or illustrations that cannot be reproduced satisfactorily by xerography.
Lee, Sam Lai

A DECOHESION MODEL OF HYDROGEN ASSISTED CRACK PROPAGATION

The Ohio State University Ph.D. 1986

University Microfilms International 300 N. Zebe Road, Ann Arbor, MI 48106
A DECOHESION MODEL OF HYDROGEN ASSISTED CRACK PROPAGATION

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of the Ohio State University

By

Sam Lai Lee, B.S., M.S.

The Ohio State University
1986

Dissertation Committee: Approved By

D.J. Unger
J.P. Hirth
J.K. Lee

Dept. of Engineering Mechanics
Co - Adviser
Dept. of Engineering Mechanics
ACKNOWLEDGEMENTS

I express sincere appreciation to Dr. D.J. Unger for his guidance and insight throughout the research. Thanks also go to the other members of my advisory committee for their suggestions and comments. Gratitude is further expressed to the Korea Advanced Energy Research Institute and the U.S. National Science Foundation for financial support.

I also offer my sincere thanks to my wife for her unshakable faith in me and her willingness to endure with me the vicissitudes of my endeavors. Additional thanks are given to my parents-in-law for their endless encouragement and financial support.
January 9, 1950 ........... Born - Chunnam, Korea

1974 ........................ B.S., Hanyang University, Seoul, Korea

1974 - 1975................ Engineer, Hyundai Motor Co., Ulsan, Korea

1976 - present ............ Research Scientist, Korea Advanced Energy Research Inst. Chungnam, Korea

1978 ........................ M.S., Brunel University London, England

1984 - 1986 ............... Graduate Research Associate, Dept. of Engineering Mech., The Ohio State University, Ohio, U.S.A.

**Fields of Study**

TABLE OF CONTENTS

ACKNOWLEDGEMENT ....................... ii
VITA ..................................... iii
LIST OF TABLES .......................... vi
LIST OF FIGURES .......................... vii
NOMENCLATURE ............................ viii
INTRODUCTION ............................ 1

CHAPTER PAGE

I. PHENOMENOLOGY AND COHESIVE ZONE GROWTH ...... 6
   Introduction .................................. 6
   Kinetic Processes ............................. 6
   Models ........................................ 8
   Growth of the Cohesive Zone .................. 9
   Results ....................................... 15

II. CRACK PROPAGATION ...................... 16
   Introduction ................................... 16
   The Kinetic Model ............................. 16
   Numerical Analysis ........................... 21
   Numerical Results ............................ 23
   Threshold Values ............................ 26

III. CONCLUSIONS ............................ 28

LIST OF REFERENCES ........................ 45

APPENDICES

A. Brief Overview of Existing Theories
   of Hydrogen Embrittlement ................. 48

B. Brief Overview of Existing Models of
   Environmental Crack Propagation ........... 51

C. Crack Opening Displacement ............... 55
D. Computer Code for Analysis of Hydrogen Assisted Crack Propagation . . . . . . . . 58
<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. A Comparison of the Approximations Used in Eq. (I.9)</td>
<td>29</td>
</tr>
<tr>
<td>2. A Comparison of Two Functions Appearing in Eq. (I.9)</td>
<td>29</td>
</tr>
<tr>
<td>3. Various Parameters</td>
<td>30</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Stress intensity versus crack velocity</td>
<td>31</td>
</tr>
<tr>
<td>2. Cohesive length, cohesive zone, cohesive force, and coordinate system</td>
<td>32</td>
</tr>
<tr>
<td>3. Infinite plate with crack subject to tensile force at infinity</td>
<td>33</td>
</tr>
<tr>
<td>4. Cohesive zone length versus time</td>
<td>34</td>
</tr>
<tr>
<td>5. Crack propagation sequence</td>
<td>35</td>
</tr>
<tr>
<td>6. Crack opening displacement versus crack length</td>
<td>36</td>
</tr>
<tr>
<td>7. A comparison of arrest and hydrogen-free crack opening displacement</td>
<td>37</td>
</tr>
<tr>
<td>8. Crack opening displacement versus time for stationary crack</td>
<td>38</td>
</tr>
<tr>
<td>9. Crack opening displacement versus crack length during crack propagation</td>
<td>39</td>
</tr>
<tr>
<td>10. Incremental crack growth</td>
<td>40</td>
</tr>
<tr>
<td>11. Variations in crack velocity versus stress intensity factor with temperature</td>
<td>41</td>
</tr>
<tr>
<td>12. Variations in crack velocity versus stress intensity factor with ( Y_C )</td>
<td>42</td>
</tr>
<tr>
<td>13. Appearance of stage II growth due to rate limiting concentration at the crack tip</td>
<td>43</td>
</tr>
<tr>
<td>14. Appearance of stage II growth due to rate limiting activation energy</td>
<td>44</td>
</tr>
</tbody>
</table>
NOMENCLATURE

\( a \) : crack length
\( \dot{a} \) : crack velocity
\( c \) : \( c = a + d \)
\( C(x,t) \) : distribution of hydrogen concentration
\( C_0 \) : crack tip hydrogen concentration
\( D \) : effective or apparent diffusivity
\( D_0 \) : pre-exponential diffusivity factor
\( d \) : cohesive zone length
\( E \) : Young's modulus
\( K_i \) : stress intensity factor
\( K_{ic} \) : plane strain fracture toughness
\( K_0 \) : additional stress intensity factor contributed by cohesive force
\( K_{th} \) : threshold stress intensity factor
\( Q \) : activation energy
\( R \) : gas constant
\( T \) : temperature
\( t \) : time
\( x \) : spatial coordinate
\( \delta \) : crack opening displacement
\( \delta_A \) : crack arrest value of crack opening displacement
\( \delta_c \) : critical value of crack opening displacement

\( \delta_e \) : elastic contribution to the crack opening displacement

\( \delta_{nc} \) : hydrogen-free crack opening displacement

\( \gamma \) : constant which relates hydrogen concentration to reduction of cohesive force

\( \nu \) : Poisson's ratio

\( \sigma_c(x,t) \) : cohesive force

\( \sigma_{c_0} \) : cohesive force in the absence of hydrogen

\( \sigma_{eff}(x,t) \) : effective cohesive force

\( \sigma_y \) : yield stress

\( \sigma_\infty \) : uniformly applied external tensile stress
INTRODUCTION

General Remarks

When a cracked specimen of a high strength steel, such as AISI 4340, is exposed to hydrogen under an applied load, subcritical crack propagation may occur. The source of hydrogen is the environment, which introduces the hydrogen to the steel either directly in the form of gas, or indirectly through a surface reaction between the metal and an aqueous solution. Hydrogen may also be introduced to a steel during the forming process or by charging a system.

A specimen which is initially free of hydrogen and which is subsequently exposed to hydrogen will pass through an incubation period before crack propagation begins. The incubation time as well as the crack velocity \( \dot{a} \) is a function of the environment, specimen geometry, crack length, and applied load. The three latter parameters can be recorded in the form of stress intensity factor \( K \), provided small scale yielding criteria are met.

Two special values of the stress intensity factor exist. A threshold stress intensity factor \( K_{th} \) below which crack propagation is not observed, and a critical
stress intensity factor $K_{IC}$ which is the plane strain fracture toughness. Typically $K_{IC}$ does not change appreciably with the environment and may be regarded as a material constant.

In the laboratory, experiments are conducted under both steady-state (time-independent) and unsteady (time-dependent) conditions. In steady-state experiments, one tries to avoid any sudden changes in $K_i$ as impulsive changes in $K_i$ produce velocity transients, and consequently time-dependent behavior. In unsteady experiments, transients in velocity are intentionally induced by step or other impulsive loads.

Three distinct stages of crack propagation are usually observed for steady-state data in plots of crack velocity versus stress intensity factor (see Fig.1). The first stage of crack growth, which is the stage nearest to $K_{IC}$, is a region exhibiting an exponential growth of $a$ in relation to $K_i$. The second stage of crack growth is a region where the crack velocity is nearly constant. The third stage of crack growth is a region close to the fracture toughness of the material $K_{IC}$. Here, the crack velocity grows very large and is again strongly dependent on $K_i$.

In unsteady experiments, contoured DCB specimens are often employed. This kind of specimen maintains a constant value of $K_i$, by virtue of its geometry, provided
the load is held constant. The stress intensity factor is therefore independent of the crack length and dependent only on the load. Transients in velocity are generated by instantaneously changing the load from one value to another. An induced velocity transient is recorded simply as a function of time, as values of $K_i$ are known before and after the step. It has been shown experimentally that all velocity transients induced by step loads eventually decay and a steady-state value of $\dot{a}$ is obtained for a specific value of $K_i$. In certain instances, an incubation period is also observed following the load change.

In [1], a study compared steady-state values of $\dot{a}$ obtained from contoured DCB specimens to steady-state values of $\dot{a}$ at the same $K_i$ obtained from more conventional specimens where $K_i$ varies during crack growth. It can be concluded from this study that some experimental data, thought to be steady-state, may actually be unsteady. Transients induced by initial loads may not always decay immediately, and the corresponding unsteady rates would be non-conservative.

Transient conditions of crack growth are often encountered in the field. The need for a model of hydrogen embrittlement that is capable of modeling both steady-state and unsteady responses is therefore evident. A successful model of hydrogen embrittlement should also be
capable of predicting incubation times, multistage growth, and time to failure. To this end, the model in this dissertation is proposed.

Scope and Objective

Hydrogen assisted cracking is an extremely complicated phenomenon, as many different kinetic mechanisms contribute to the overall degradation process. To complicate matters further, many details of the physics and the chemistry of these individual mechanisms are simply unknown. Indeed the fundamental question of why hydrogen embrittles steel is still largely unanswered (see Appendix A). This problem is further compounded by other uncertainties related to fluid transport, surface reactions, adsorption kinetics, stress-assisted diffusion, and trapping mechanisms. Nevertheless, the ever increasing demands of modern technology dictate that hydrogen assisted cracking be better quantified in the form of a model.

We can find some encouragement in the task of developing a model of hydrogen assisted cracking from similar problems that have been overcome in modeling plasticity and fatigue. These phenomena are also related to time- and path-dependent microstructural processes. Nonetheless engineers have been able to quantify these processes through the use of
phenomenological models.

At present relatively few models of hydrogen assisted cracking have been developed. The few models that do exist have many undefined parameters, which consequently limit their predictive capability. Furthermore, most of the existing models do not allow for time dependent mechanisms, and most assume conditions of equilibrium. Neither of these assumptions should be universally accepted.

The development of a phenomenological model of hydrogen assisted cracking that is applicable to both steady and unsteady phenomena, predicts incremental crack propagation and incubation periods, and which allows for multistage crack propagation is the objective of this dissertation.
CHAPTER I

PHENOMENOLOGY AND COHESIVE ZONE GROWTH

Introduction

In this chapter, we discuss some kinetic processes associated with hydrogen assisted crack propagation. We further discuss some previous models on which the present model builds, and then propose a new decohesion model of cohesive zone growth.

Kinetic Processes

A number of kinetic processes may be operating simultaneously in subcritical cracking associated with hydrogen embrittlement, any one or a combination of which may be rate limiting and produce the stage II growth noted earlier. Fluid transport, for example can be a rate limiting process. A deleterious substance, be it a gas or a liquid, must migrate from its environmental reservoir to a region near the crack tip. If the supply cannot meet the demands of the embrittling process, the overall process is rate limited.

In the case of a liquid, chemical reactions which occur near the crack tip to produce hydrogen gas can also
be rate limiting. For example, in the case of water or water vapor and AISI 4340 steel, a chemical reaction associated with the oxidation of metal and release of hydrogen gas has been identified [2].

Once hydrogen gas has reached the outer surface of the crack tip from an external source, it must enter the metal by an adsorption process. The first type is a physical adsorption of hydrogen gas, where molecules as opposed to atoms are adsorbed. The second type is called chemisorption where molecules dissociate into atoms because of a strong crystalline field [3]. At low temperatures the first can be rate limiting and at room temperature the second can be rate limiting as indicated by studies involving hydrogen gas and AISI 4340 steel [4].

Upon entering the material, the hydrogen diffuses under the influence of hydrostatic stress gradients. In [5], crack growth controlled by the internal diffusion of hydrogen in AISI 4340 steel exposed to an environment of hydrogen sulfide gas has been reported. Hydrogen which has been introduced into the matrix of the metal by the forming process or by charging [6] must also diffuse to reach the neighborhood of the crack tip. Mobile dislocations can also carry hydrogen clouds [7] to increase the apparent diffusivity. Traps such as voids, dislocations, grain boundaries, and foreign atoms can serve as local sources or sinks of hydrogen.
Models

The model of embrittlement presented here is based on the concept of a degrading cohesive force. This mechanism of hydrogen embrittlement was previously proposed by Troiano [8] and his coworkers. It was later applied by Oriani and Josephic [9] to the modeling of threshold data for AISI 4340 steel in hydrogen gas. The model in [9] assumed that the cohesive force between atoms is lowered in a linear fashion with the concentration of hydrogen. No exact relationship is known between the concentration of hydrogen and loss of cohesive force. However, if one assumes that the cohesive force is a function of the hydrogen concentration, then the first two terms of a Taylor series expansion of the cohesive force are indeed linear in the concentration. As such, this seems to be a reasonable first approximation.

The analysis in [9], though, is limited in that it cannot be applied to stages of crack growth beyond $K_{1c}$, nor can it model time-dependent behavior.

A different decohesion model of hydrogen embrittlement was proposed by Neimitz and Aifantis [10] and [11]. There a Barenblatt zone of cohesive force which degrades and extends with time due to the presence of hydrogen was introduced. Crack initiation and arrest were based on crack opening displacement criteria. The crack opening displacement was assumed to be a function of
the average concentration of hydrogen, which is in turn a function of time.

With the introduction of a subcritical fracture criteria based on an evolving parameter, time-dependent (unsteady) crack propagation could be modeled for the first time.

The model proposed here builds upon the groundwork of the models in [9], [10], and [11]. Its origin lies in a preliminary model found in [12]. For other models of environmentally assisted cracking, the reader is referred to Appendix B.

Growth of the Cohesive Zone

We will now begin the formulation of our model. Our first task will be to establish the growth of the cohesive zone. In chapter II [13] of this dissertation, we will show that this growth is concurrent with an increase in the crack opening displacement, which will ultimately provide a measure of the damage due to the presence of hydrogen in the metal. Although a specific boundary value problem for a particular initial condition will be analyzed in this section, it must be kept in mind that this model can be readily modified to include others. The kinetic model for a propagating crack proposed in Chapter II, will be consistent with the model presented here for the growth of the cohesive zone, and it will be
able to predict incubation times, an initiation criterion, and multistage crack propagation. The kinetic processes mentioned in a previous section can also be incorporated into the kinetic model.

In a Barenblatt model, the cohesive force provides an additional contribution to the stress intensity factor so that the total stress intensity factor remains zero. This assumption is based on the physical assumption that stresses at the crack tip should remain finite. If we denote this additional contribution due to the cohesive force with the symbol \( K_0 \) then this condition reads

\[
K_0 + K_1 = 0 \hspace{1cm} \text{(I.1)}
\]

where \( K_1 \) is identified as the usual elastic or mechanical component of the stress intensity factor. To determine \( K_0 \) one must substitute an expression for the cohesive force(stress) \( \sigma_c(x,t) \) into the following integral [14]

\[
K_0 = -2(c/\pi)^{1/2} \int_a^c \frac{\sigma_c(x,t)}{(c^2 - x^2)^{1/2}} \, dx \hspace{1cm} \text{(I.2)}
\]

where \( x \) is the coordinate shown in Fig.2, \( a \) is crack length, \( t \) is time, and \( c = a + d \) where \( d \) is the length of the cohesive zone.
The cohesive force is, in general, a function of the distance between atoms (idealized as surfaces) between a and c. However, in order to isolate the qualitative effect of the hydrogen concentration on the degradation of the cohesive force and to simplify the analysis, we will assume that the cohesive force is independent of the displacement of the crack surfaces. In conformity with this assumption, the cohesive force before the introduction of hydrogen is constant.

The cohesive force will now be assumed to be linearly degraded by concentration of hydrogen $C(x,t)$

$$\sigma_c(x,t) = \sigma_{c_0} - \gamma C(x,t) \quad \quad \quad \quad (I.3)$$

where $\sigma_{c_0}$ is the cohesive force in the absence of hydrogen, and $\gamma$ is a constant. For this particular analysis we will further assume that the initial concentration of hydrogen $C(x,0)$ is zero. Thus we are modeling hydrogen embrittlement that is introduced from the environment, as opposed to hydrogen that is initially present in the specimen. At time $t = 0^+$ a constant concentration of hydrogen $C_0$ is imposed at the crack tip. The concentration of hydrogen will be governed by the heat equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad \quad \quad \quad (I.4)$$
where $D$ is the diffusivity. The use of the heat equation in Eq. (I.4) represents the simplest possible model of hydrogen diffusion, although the model itself is not innately restricted to this equation. Equation (I.4) can be replaced by a stress-assisted diffusion equation such as that proposed in [15]. Here we are trying to establish only qualitative behavior due to the decohesion mechanism. As such $D$ in Eq. (I.4) should be understood as representing an apparent or effective diffusivity.

The solution of the heat equation in one dimension for an initial concentration of hydrogen equal to zero and for a constant boundary condition $C_0$ follows

$$C(x, t) = C_0 (1 - \text{erf} \left( \frac{x-a}{(4Dt)^{1/2}} \right)) \ldots (I.5)$$

where erf ( ) is the error function.

For the purpose of this analysis, let us now assume that the stress intensity factor is that of an infinite plate subject to a tensile load $\sigma_\infty$ on the outer boundary (see Fig. 3), i.e.

$$K_1 = \sigma_\infty (\pi c)^{1/2} \ldots \ldots \ldots \ldots \ldots \ldots \ldots (I.6)$$

The substitution of Eqs. (I.2), (I.3), (I.5), and (I.6) into Eq. (I.1) gives the Barenblatt condition as
Now the first part of integral Eq.(1.7) may be readily evaluated to give

\[
\int_{0}^{c} \left( \sigma_{c} - \gamma C_{0} \right) \cos^{-1} \left( \frac{a}{c} \right) + \gamma C_{0} \int_{a}^{c} \text{erf} \left[ \frac{(x-a)/(4Dt)^{1/2}}{(c^2-x^2)^{1/2}} \right] dx
\]

\[
= \frac{\pi}{2} \sigma_{00}. \quad \text{(I.7)}
\]

The remaining integral in Eq.(I.8) may be approximated by formula 25.4.37 given in [16] to yield

\[
\left( \sigma_{c} - \gamma C_{0} \right) \cos^{-1} \left( \frac{a}{c} \right) + 2\gamma C_{0} \left( \frac{3(c-a)}{5c+a} \right)^{1/2} \text{erf} \left[ \frac{(c-a)/(9Dt)^{1/2}}{1} \right]
\]

\[
= \frac{\pi}{2} \sigma_{00}. \quad \text{(I.9)}
\]

This one term approximation is quite satisfactory for analyzing qualitative behavior. Comparisons between the one term approximation, a ten term approximation, and a twenty term approximation are shown in Table 1 and Fig.4. We can see a twenty term approximation is virtually indistinguishable from the ten term approximation.
Table 2 shows how closely two different functions appearing in Eq. (1.9) agree for c/a. Therefore, in Eq. (1.9) we can replace the second function appearing in the table by the first with little loss in accuracy. This leads to the following convenient form which replaces Eq. (1.9)

\[
\cos^{-1}(a/c) = \left( \frac{\pi}{2} \right) \sigma_\infty / \left( \sigma_c - \gamma C_0 + \gamma C_0 \text{erf}[(c-a)/(9Dt)^{1/2}] \right)
\]  

... (I.10)

Now we take the cosine of both sides of Eq. (I.10) to obtain

\[
a/c = \cos\left( \frac{\pi}{2} \right) \sigma_\infty / \left( \sigma_c - \gamma C_0 + \gamma C_0 \text{erf}[(c-a)/(9Dt)^{1/2}] \right)
\]

... (I.11)

Let us now define an effective cohesive force

\[
\sigma_{c,eff} = \sigma_c - \gamma C_0 \text{erfc}[(c-a)/(9Dt)^{1/2}]
\]

... (I.12)

using the complementary error function, \( \text{erfc}(x) = 1 - \text{erf}(x) \). By rearranging Eq. (I.11) and by substituting Eq. (I.12) into Eq. (I.11) we find

\[
c/a = \sec(\pi \sigma_\infty / (2 \sigma_{c,eff}))
\]

... (I.13)

Equation (I.13) has a familiar form found in fracture mechanics literature. An expression similar to Eq. (I.13) has been used to determine the length of a
plastic zone c (Dugdale model), where the time-dependent 
\(\sigma_{c,\infty}\) is replaced by a constant yield stress \(\sigma_y\) [17].

Being a function of time, however, one finds that Eq. (1.13) predicts a monotonically increasing cohesive zone instead of a constant length as in the Dugdale model.

**Results**

Requirements for a successful model of hydrogen embrittlement have been discussed. A model which predicts a monotonically increasing cohesive zone due to the presence of hydrogen is presented as a precursor to such a model.
CHAPTER II
CRACK PROPAGATION

Introduction

In chapter I [18] of this dissertation, the candidate described some phenomenological aspects of hydrogen assisted cracking. He also advocated the use of a decohesion model of hydrogen embrittlement where a Barenblatt zone of cohesive force degrades linearly in relation to the concentration of hydrogen. In this model, the cohesive zone grows to compensate for the loss of cohesion subject to the Barenblatt (finite stress) condition. A simple boundary value problem was formulated where hydrogen diffusing from the environment into a specimen initially free of hydrogen resulted in a monotonically increasing cohesive zone. In this chapter the candidate will introduce into the model criteria of crack initiation and arrest. He will also discuss the incorporation of various rate limiting kinetic processes, and the model’s multistage crack growth capability.

Kinetic Model
Figure 5a shows a schematic representation of the initial conditions of a typical specimen exposed to hydrogen [18]: an initial crack length $a_0$, an initial cohesive zone length $d_0$, and a constant cohesive force $\sigma_c$. The specimen is assumed initially free of hydrogen with a boundary condition of hydrogen concentration $C_0$ imposed at the crack tip.

Figure 5b represents an early stage of material degradation. The material has been damaged by hydrogen diffusing from the crack tip. The cohesive zone extends due to the degraded cohesive force subject to the Barenblatt condition, Eq.(1.1).

The crack opening displacement $\delta$ will now be proposed as the damage criterion for this model.

In general, the crack opening displacement can be calculated numerically using Eq.(2.3.13) found in [14], a double integration over the cohesive force $\sigma_c$, plus an elastic contribution. Accordingly, we have

$$\delta = -\Lambda \int_a^c \frac{x}{(x^2 - c^2)^{1/2}} \int_a^x \sigma_c(t, \xi)/(x^2 - \xi^2)^{1/2} d\xi \, dx \, \delta_0 \, . \quad \text{(II.1)}$$

such that

$$\Lambda = \begin{cases} \delta(1 - \nu^2)/(\pi E) & \text{for plane strain}, \\ \delta/(\pi E) & \text{for plane stress} \end{cases}$$

where $E$ is Young's modulus, $\nu$ = Poisson's ratio, $x$ is the spatial coordinate, $t$ is time, and $c = a + d$. The term
In Eq. (II.1) is the elastic contribution to the crack opening displacement whose form is dependent on the geometry of the specimen and load. For example, an infinite plate with a crack length of 2a subject to a tensile force $\sigma_0$, as shown in Fig. 3, has

$$\delta_e = \frac{1}{2}(\pi/2) \frac{\sigma_0 (c^2-a^2)^{1/2}}{a}$$ \hspace{1cm} (II.2)

At the early stage of degradation represented in Fig. 5b (see the corresponding point (b) in Fig. 6), the cohesive zone has extended to the length $d_1$, but the crack opening displacement is below a postulated critical value $\delta_c$ where subcritical crack propagation begins. For the present, it is assumed that $\delta_c$ is constant, i.e. free of environmental and material effects. However, variable criteria can be readily introduced into the model.

In Fig. 5c (point (c) in Fig. 6), the degradation of the cohesive force has reached a state where crack propagation initiates, i.e. where the crack opening displacement has grown to the critical value, $\delta = \delta_c$. The time it takes to reach this state from the corresponding state shown in Fig. 5a may be interpreted as the incubation time.

We know that as the crack tip advances it moves from very damaged material into much healthier material over a short distance. In the healthier material, the cohesive
force is near its original strength and consequently subcritical growth is initially accompanied by a drop in $\delta$ as the material is experiencing a large effective increase in cohesive force. However, the crack opening displacement cannot continue to fall indefinitely with crack advance. Once the bulk of the hydrogen damage has been passed, the effective cohesive force becomes essentially constant and any increase in crack length is subsequently accompanied by an increase in $\delta$, as is normally observed under inert conditions. This transition is represented by a solid line in Fig. 6, and represents a natural lower bound for $\delta$ which we will term $\delta_a$.

Figure 5d (point (d) in Fig. 6) shows a crack that has arrested. It is proposed that the crack arrests when the crack opening displacement falls to $\delta_a$. To find the new crack length $a$, and the new cohesive zone length $d$, subject to the Barenblatt condition and Eq. (II.1), requires a numerical procedure.

It is assumed that the time it takes to go from crack initiation shown in Fig. 5c to crack arrest shown in Fig. 5d is very short. As no significant time passed between crack initiation and arrest, the hydrogen concentration profile in Fig. 5d is the same as in Fig. 5c. However, only the hydrogen beyond the new crack tip $a_c$ contributes to the subsequent degradation of the material, i.e. the initial concentration of hydrogen for the second increment
of crack growth. For the most part, it is believed that this remnant of hydrogen is very small.

We are now faced with the problem of imposing a new boundary condition of hydrogen concentration at the new crack tip at \( x = a \). If we assume that the kinetic processes which supply the hydrogen to the crack tip are not rate limiting, then imposing the same concentration \( C_0 \) as before is not an unreasonable assumption. As we are concentrating on the decohesion mechanism for the present, let us assume this particular assumption holds.

In Fig. 5e (point (e) in Fig. 6), a state is shown where the cohesive zone and crack opening displacement are again expanding due to the hydrogen decohesion following the first increment of crack advance. The hydrogen from the state shown in Fig. 5d remained as the initial concentration profile, and the boundary condition \( C_0 \) has been imposed at the new crack tip \( a \). The crack is not presently moving as \( \delta \) is temporarily below \( \delta_c \).

A cycle of subcritical crack initiation and arrest will then follow until the crack grows to a length where \( \delta_a \) coincides with \( \delta_c \). At this point, the crack opening displacement is forced to rise above \( \delta_c \) and instantaneous failure occurs. This critical point (f) is shown in Fig. 6.

Average crack velocities can be calculated by dividing the increment of crack growth by the increment of
time between subcritical crack initiations. The shortening path shown in Fig. 6 causes monotonically increasing crack velocities.

Numerical Analysis

A computer code was developed to test the qualitative behavior of the model described in the previous section.

The computer program used an analytic solution, Eq. (I.5) of the diffusion equation, Eq. (I.4) to quantify the evolution of hydrogen in the specimen. After each increment of crack growth, the time and initial concentration of hydrogen were reset to zero for the next increment of crack growth. This is a reasonable assumption as the crack will advance into very healthy material with each increment of crack growth. Very little hydrogen actually remains to affect the subsequent cohesive zone strength.

As the hydrogen content in the specimen increases with time, the code calculates corresponding cohesive zone lengths and crack opening displacements. The cohesive zone must be determined using Eq. (I.1), followed by the crack opening displacement using Eq. (II.1). The numerical integrations of Eq. (II.1) and the inner integral of Eq. (II.1) employed Eq. (25.4.37) of [16] and ten Gaussian weights. This numerical integration scheme was chosen as it allows naturally for the square root singularities.
encountered in the integrations. A Romberg integration scheme DCADRE which is an International Mathematics and Statistical Libraries (IMSL) subroutine was used for the outer integration of Eq. (II.1).

The computer code uses an incremental, path-dependent procedure. Using small increments of time the program determines when the crack opening displacement first reaches \( \delta_c \) from its initial state. The crack length \( a \) is then allowed to grow in very small increments. The cohesive zone length and crack opening displacement are calculated for each small increase in crack length. When the crack opening displacement falls to \( \delta_a \), the crack arrests. The value \( \delta_a \) is actually determined numerically and occurs when \( \delta \) begins to increase with the crack length. It was discovered numerically that it approaches the hydrogen-free crack tip opening displacement

\[
\delta_{wC} = \Lambda \sigma_c \ln[\sec(\pi \sigma_c/(2 \sigma_c))] \ldots \ldots \quad (II.3)
\]

A representative comparison is shown in Fig.7. The close proximity of these two curves suggests that little residual hydrogen remains to affect subsequent crack growth. For a derivation of Eq. (II.3), see Appendix C.

Average crack velocities are calculated by dividing increments of crack growth by increments of time between critical events. Only the time between the previous
arrest and the new initiation is considered. The small amount of time which passes during the actual propagation is ignored.

The external load \( \sigma_0 \) is held constant in the program and the stress intensity factor \( K_i \) for an infinite plate shown in Fig.3 is used.

**Numerical Results**

In Figs. 8 and 9 the crack opening displacement is plotted. As expected, it increases with time before attaining the critical value \( \delta_c \) (Fig.8), and it decreases with crack length following the attainment of \( \delta_c \) (Fig.9). A plot of crack length versus time in Fig.10 shows the incremental nature of subcritical crack propagation.

In Fig. 11, crack velocities are plotted for a variation of temperature (270°K - 377°K) on semi-log paper. Here, \( Y C_0 \) was chosen to be 0.65 \( \sigma_c \) and \( C_0 \) was chosen as 23Ksi. A summary of other parameters that were used in the calculation are given in Table 3. Note that the diffusivity has an Arrhenius representation

\[
D = D_0 \exp\left(-\frac{Q}{RT}\right) \quad \ldots \ldots \ldots \ldots \ldots \quad (II.4)
\]

where \( Q \) is the activation energy, \( R \) is the gas constant, \( T \) is absolute temperature, and \( D_0 \) is a constant. Fig.11 shows behavior that closely resembles the three stages of
crack growth behavior as shown in Fig. 1.

Two curves are plotted in Fig. 12 for a constant temperature of 295°K: a curve where solid circles represent data points for the case $\gamma C_0 = 0.65 \sigma_0$, and a curve where hollow circles represent data points for the case $\gamma C_0 = 0.9 \sigma_0$. We note that the curves plotted in Fig. 12 again exhibit what appear to be all three stages of steady-state crack growth behavior. We also find that crack velocities increase with $\gamma C_0$, i.e. with an increase in the degradation of cohesive force by hydrogen.

Note that we have chosen a value of initial cohesive stress that is approximately the yield stress of an AISI 4340 steel. With this stress, and the calculation of a critical crack opening displacement based on a plane strain Dugdale model, we can obtain stage III growth as we approach $K_{IC}$. Naturally, this "cohesive force" must be interpreted as an effective cohesive force rather than the actual as it is about 15 times less than the theoretical strength $E/10$. As we are ignoring the details of the process zone, which to a large extent are unknown, this seems a reasonable phenomenological approach.

Stage II crack growth behavior which is nearly independent of the stress intensity factor, as shown in Fig. 1, is not observed in Figs. 11 or 12. This might be expected as stage II growth is also attributed to rate limiting kinetic processes (see Chapter I) that are not
Incorporated into this code.

Kinetic processes can make the boundary condition \( C_0 \) a function of time, crack length, crack velocity, and other variables. Overall, these processes might tend to lower \( YC_0 \) as the crack grows. We can demonstrate one possible effect of these processes on crack velocities, by using for \( YC_0 \), the following function which decreases with crack length

\[
YC_0(a) = 0.80 \sigma_w - (0.2 \sigma_w/\pi) \tan^{-1} \left( \left( \sigma_w/\pi \right)^{1/2} - K_* \right) \]  \hspace{1cm} (II.5)

where \( \sigma_w = 1.5 \times 10^{-2} / (Ksi \text{in})^{1/2} \) and \( K_* = 30 \text{Ksi(in)}^{1/2} \).

Figure 13 shows velocity curves plotted as functions of \( K_i \) at different temperatures, where \( YC_0 \) decreased according to Eq. (II.5). The appearance of plateau regions in these curves demonstrates stage II growth can be affected from changes in the boundary condition \( C_0 \). Naturally the actual function \( YC_0 \) should be determined from the governing equations of the specific rate limiting mechanisms that are operating. We have provided this example only to show that stage II growth can be enhanced through a decrease in hydrogen concentration at the crack tip with crack growth.

We might add that in addition to the boundary condition \( C_0 \), the appearance of plateau regions in stage II crack growth can result from changes of activation
energy. In some cases, this change of activation energy can be attributed to the microstructure. Figure 14 shows results obtained by a constantly increasing activation energy of the form

$$Q(a) = Q_1 + \left(\frac{600}{\pi} \right) \tan^{-1}\left(\frac{\epsilon}{(\sigma_0)^{1/2}} \right) \text{ J/mol}$$

where

$$Q_1 = 1.21 \times 10^5 \text{ J/mol}, \quad \epsilon = 1.5 \times 10^{-3} \text{ /(Ksi(in))}^{1/2}$$

and

$$K_0 = 36.0 \text{ KSi(in)}^{1/2}.$$

Finally, we note that the changes which occur in the curves in the various figures with temperature are in conformity with most experimental trends. For those mechanisms which do not allow an Arrhenius representation, an alternate relationship can be substituted in place of Eq.(II.4).

Threshold Values

As time goes to infinity the cohesive force $\sigma_c(x, t)$ will become the constant $(\sigma_c^0 - \gamma C_0)$ in our model. This is indicated by Eqs. (1.3) and (1.5). As the cohesive force becomes a constant as $t \to \infty$, the corresponding $\delta$ is readily calculated analytically (see Appendix C) as

$$\delta_\infty = \Lambda \sigma_c^0 (\sigma_c^0 - \gamma C_0) \ln \left( \sec \left( \frac{\pi}{2} \frac{\sigma_0}{(\sigma_c^0 - \gamma C_0)} \right) \right). \quad (II.6)$$
which is approximately

$$\delta_\infty = (1-\nu^2) K_0^*/[E (\sigma_{c0} - \gamma C_0)] \ldots \ldots (II.7)$$

for plane strain conditions with $\sigma_\infty \ll (\sigma_{c0} - \gamma C_0)$. The crack opening displacement $\delta_\infty$ represents the largest value of $\delta$ that a stationary crack can potentially reach. If $\delta_\infty$ is less than $\delta_c$ the crack will never propagate. If $\delta_\infty$ is greater than $\delta_c$ the crack will begin to propagate before $\delta_\infty$ is ever reached. The case $\delta_\infty$ equals $\delta_c$ corresponds to a threshold condition.

Now $K_{th}$ represents the lowest value of stress intensity factor for which a crack will begin to propagate assuming fixed environmental conditions. We can find $K_{th}$ by setting $\delta_\infty = \delta_c$ in Eq. (II.7) and by solving for $K_0$ to obtain

$$K_{th} = \left[ \frac{\delta_c E (\sigma_{c0} - \gamma C_0)/(1-\nu^2)}{(1-\nu^2)} \right]^{1/2} \ldots \ldots (II.8)$$

Note that a value of $K_{th}$ obtained from a threshold experiment will determine $\gamma C_0$, as the rest of the parameters are presumed known from hydrogen-free tests.
CHAPTER III

CONCLUSIONS

A model of hydrogen assisted cracking has been formulated that predicts incremental crack growth. It also allows for crack propagation to initiate at a realistic $K_I$, and for failure to occur at realistic $K_{IC}$. Between these limits we have demonstrated that all three stages of steady-state crack propagation are possible within the existing framework of the model.

Many kinetic mechanisms due to microstructure and internal diffusion can be reflected through the apparent diffusivity $D$. External fluid transport and adsorption mechanisms can be reflected through the parameter $C_0$.

Overall the candidate is quite enthusiastic about the potential of this new model.
Table 1
A Comparison of the Approximations Used in Eq. (I.9)

<table>
<thead>
<tr>
<th>time (sec)</th>
<th>c/a (*)</th>
<th>c/a (**)</th>
<th>c/a (***)</th>
</tr>
</thead>
<tbody>
<tr>
<td>105</td>
<td>1.04983</td>
<td>1.05231</td>
<td>1.05296</td>
</tr>
<tr>
<td>205</td>
<td>1.06052</td>
<td>1.06280</td>
<td>1.06237</td>
</tr>
<tr>
<td>305</td>
<td>1.06806</td>
<td>1.07025</td>
<td>1.07058</td>
</tr>
<tr>
<td>405</td>
<td>1.07406</td>
<td>1.07620</td>
<td>1.07637</td>
</tr>
<tr>
<td>505</td>
<td>1.07912</td>
<td>1.08123</td>
<td>1.08146</td>
</tr>
<tr>
<td>605</td>
<td>1.08354</td>
<td>1.08562</td>
<td>1.08583</td>
</tr>
<tr>
<td>705</td>
<td>1.08748</td>
<td>1.08955</td>
<td>1.08973</td>
</tr>
<tr>
<td>805</td>
<td>1.09072</td>
<td>1.09311</td>
<td>1.09328</td>
</tr>
</tbody>
</table>

(*) : single term approximation
(***): 10 term approximation
(****): 20 term approximation

Table 2
A Comparison of Two Functions Appearing in Eq. (I.9)

<table>
<thead>
<tr>
<th>c/a</th>
<th>arccos(a/c)</th>
<th>2[3(c-a)/(5c+a)]^{-1/2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.000000</td>
<td>0.000000</td>
</tr>
<tr>
<td>1.01</td>
<td>0.140836</td>
<td>0.140836</td>
</tr>
<tr>
<td>1.05</td>
<td>0.309845</td>
<td>0.309839</td>
</tr>
<tr>
<td>1.10</td>
<td>0.429700</td>
<td>0.429669</td>
</tr>
<tr>
<td>1.20</td>
<td>0.585686</td>
<td>0.585540</td>
</tr>
<tr>
<td>2.00</td>
<td>1.047198</td>
<td>1.044666</td>
</tr>
<tr>
<td>10.00</td>
<td>1.470629</td>
<td>1.455214</td>
</tr>
<tr>
<td>∞</td>
<td>1.570796</td>
<td>1.549193</td>
</tr>
</tbody>
</table>
Table 3

Various Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>$29.15 \times 10^4$ Psi, $\nu = 0.25$</td>
</tr>
<tr>
<td>$K_c$</td>
<td>$42$ Ksi/(in)$^{1/2}$, $\sigma_y = 1.9 \times 10^5$Psi</td>
</tr>
<tr>
<td>$a_0$</td>
<td>$0.4$ in., $\varepsilon_c = 0.2986 \times 10^{-3}$ in.</td>
</tr>
<tr>
<td>$D_b$</td>
<td>$100$ cm$^2$/s, $Q = 1.18 \times 10^4$ J/mol</td>
</tr>
<tr>
<td>$R$</td>
<td>$1.9875$ cal/mol/$^\circ$K</td>
</tr>
</tbody>
</table>
Fig. 1 Stress intensity versus crack velocity
Fig. 2 Cohesive length, cohesive zone, cohesive force, and coordinate system
Fig. 3 Infinite plate with crack subject to tensile force at infinity
COHESIVE ZONE LENGTH $\times 10$ in.

$E = 29.15 \times 10^4$ Psi

$K_{IC} = 42 \text{ ksi}(\text{in})^{1/2}$

$a_0 = 0.4 \text{ in.}$

$\nu = 0.25$

$\sigma_Y = 1.9 \times 10^3$ Psi

$\delta_c = 0.2986 \times 10^{-3}$ in.

Fig. 4 Cohesive zone length versus time
Fig. 5 Crack propagation sequence
Fig. 6 Crack opening displacement versus crack length
CRACK OPENING DISPLACEMENT $\times 10^3$ in.

CRACK LENGTH, inch

Fig. 7 A comparison of arrest and hydrogen-free crack opening displacement

- $E = 29.15 \times 10^4$ Psi
- $K_{ic} = 42$ ksi(in)$^{1/2}$
- $a_0 = 0.4$ in.
- $Q = 1.18 \times 10^4$ J/mol
- $R = 1.9875$ cal/mol/°K
- $\nu = 0.25$
- $\sigma_y = 1.9 \times 10^3$ Psi
- $\delta_c = 0.2986 \times 10^{-3}$ in.
- $D_0 = 100$ cm$^2$/sec
Fig. 8 Crack opening displacement versus time for stationary crack

- $E = 29.15 \times 10^6$ Psi
- $K_{tc} = 42$ KSI(in)$^{1/2}$
- $a_0 = 0.4$ in.
- $Q = 1.18 \times 10^4$ J/mol
- $R = 1.9875$ cal/mol/$^0$K
- $\nu = 0.25$
- $G_0 = 1.9 \times 10^3$ Psi
- $\delta_0 = 0.2986 \times 10^{-3}$ in.
- $D_0 = 100$ cm$^2$/sec
Fig. 9 Crack opening displacement versus crack length during crack propagation
Temp: 323 K

\[ Y_G = 0.65 G_0 \]

\[ G_0 = 23 \text{ ksi} \]

\[ E = 29.15 \times 10^8 \text{ Psi} \]

\[ K_{IC} = 42 \text{ ksi (in)}^{1/2} \]

\[ a_0 = 0.4 \text{ in.} \]

\[ Q = 1.18 \times 10^9 \text{ J/mol} \]

\[ R = 1.9875 \text{ cal/mol}^{{1/2}}K \]

\[ \gamma = 0.25 \]

\[ G = 1.9 \times 10^9 \text{ Psi} \]

\[ D_0 = 0.2986 \times 10^{-4} \text{ in.} \]

\[ D_0 = 100 \text{ cm}^2/\text{sec} \]

**Fig. 10 Incremental crack growth**
Fig. 11 Variations in crack velocity versus stress intensity factor with temperature

\[ \frac{Yc_o}{c_o} = 0.65c_o \]

\[ f_P = 23 \text{ ksi} \]

\[ K_{1c} = 42 \text{ ksi}(\text{in})^{1/2} \]

\[ a_o = 0.4 \text{ in.} \]

\[ Q = 1.18 \times 10^4 \text{ J/mol} \]

\[ R = 1.9875 \text{ cal/mol/°K} \]

\[ \nu = 0.25 \]

\[ f_P = 1.9 \times 10^8 \text{ Pa} \]

\[ \Omega = 0.2986 \times 10^{-2} \text{ in.} \]

\[ D_o = 100 \text{ cm}^2/\text{sec} \]
Temp: 295 K

A: \( \gamma C_0 = 0.9 \sigma_0 \)
\[ \alpha = 15 \text{ksi} \]

B: \( \gamma C_0 = 0.65 \sigma_0 \)
\[ \alpha = 23 \text{ksi} \]

\[ E = 29.15 \times 10^4 \text{ Psi} \]
\[ K_{IC} = 42 \text{ Ksi(in)}^{1/2} \]
\[ \rho_0 = 0.4 \text{ in.} \]
\[ Q = 1.18 \times 10^6 \text{ J/mol} \]
\[ R = 1.9875 \text{ cal/mol/°K} \]
\[ \nu = 0.25 \]
\[ \sigma_f = 1.9 \times 10^9 \text{ Psi} \]
\[ \delta_0 = 0.2986 \times 10^{-2} \text{ in.} \]
\[ D_0 = 100 \text{ cm}^4 / \text{sec} \]

Fig. 12 Variations in crack velocity versus stress intensity factor with \( \gamma C_0 \)
Fig. 13 Appearance of stage II growth due to rate limiting concentration at the crack tip
Fig. 14 Appearance of stage II growth due to rate limiting activation energy

\[ R = 1.9875 \text{ cal/mol/°K} \]
\[ \nu = 0.25 \]
\[ Q_0 = 1.9 \times 10^6 \text{ Psi} \]
\[ b = 0.2936 \times 10^{-5} \text{ in.} \]
\[ D_0 = 100 \text{ cm}^2/\text{sec} \]

\[ E = 29.15 \times 10^6 \text{ Psi} \]
\[ K_t = 42 \text{ Ksi(in)}^{1/2} \]
\[ a_0 = 0.4 \text{ in.} \]

\[ Y_{CA} = 0.65G_0 \]

\[ G_0 = 23 \text{ Ksi} \]

\[ Q(a) = Q \times (600/\pi) \tan^{-1} \]
\[
(\frac{Q_0(\sigma a)^{1/2}}{K_0})
\]

\[ G = 1.21 \times 10^5 \text{ J/mol} \]
\[ ( = 1.5 \times 10^{-3} \text{/Ksi(in)}^{1/2} \text{ in}) \]

\[ K_c = 36.0 \text{ Ksi(in)}^{1/2} \]
LIST OF REFERENCES


21. Wiederhorn, S.M., "Influence of Water Vapor on Crack
Propagation in Soda-Lime Glass."


A review about existing theories of hydrogen embrittlement is given by Hirth [19]. In his review, seven distinct theories were identified. Here we give a short review of each.

a) Transport Theory

Although not a theory per se, hydrogen transport plays an important role in the embrittlement of steel. Hydrogen may be transported as a fluid, undergo adsorption and absorption, diffuse internally, be carried along with mobile dislocations, and be trapped by lattice inhomogeneities.

b) Internal Pressure Theory

The internal pressure mechanism is based on the concept of large internal hydrogen pressures in voids. However, this mechanism cannot be universally accepted because crack propagation also occurs at subatmospheric pressures. At room temperature, void growth is possible
by pressure enhancement, but only for high fugacity environments. However, at low temperatures, large supersaturations (and consequently high pressures) in voids are possible through dislocation transport of hydrogen.

c) Slip Softening Model

This model is based on the concept that hydrogen enhances dislocation motion. However, this idea can be criticized because hardening effects are also observed. Enhanced dislocation motion, though, remains a possible contributing factor to the overall hydrogen embrittlement process.

d) Surface Energy

This model is basically same as Griffith crack propagation model. Here surface energy and consequently the work of fracture is lowered by hydrogen adsorption. However, this model does not explain certain phenomena such as incremental crack growth. It also underestimates the fracture work, and fails to explain why oxygen does not enhance embrittlement.

e) Brittle Crack Tip

This theory assumes that cracking can occur in a locally irreversible brittle fashion by thermal or athermal activation over the lattice trapping barrier related to an
atomically sharp crack tip. At present, an accurate hydrogen-iron atomic interaction potential is lacking. This prevents the necessary calculations needed to estimate the effect of hydrogen on the lattice trapping barrier.

f) Hydrogen Formation

This theory proposes that crack propagation is the result of the formation and subsequent cracking of a hydride near the crack tip. It assumes the hydride is stabilized by the hydrostatic stress field. However, no hydride is stable until pressures of 2 Gpa are applied. Thus this model has not been accepted for hydrogen embrittlement of steel.

g) Decohesion Theory

This theory assumes that the cohesive forces between atoms in steel are lowered by the presence of hydrogen.
APPENDIX B

BRIEF OVERVIEW OF EXISTING MODELS
OF ENVIRONMENTAL CRACK PROPAGATION

An early attempt to quantify steady-state crack velocity as a function of the applied stress in the presence of an aggressive environment was the work of Charles and Hilig [20]. These investigators made the assumption of an Eyring rate-type relationship of the following form

\[ \dot{a} = v_0 \exp(\beta \sigma) \] .......................... (A.1)

where \( \dot{a} \) is the velocity of the crack tip, \( v_0 \) and \( \beta \) are phenomenologically determined coefficients, and \( \sigma \) is the applied stress. This relationship (A.1) was based on the assumption that activation energy is proportional to the stress. Experimentally, a relationship of this type fits data very well for stress corrosion cracking of glass in water [20] and [21]. For temperature variations, the coefficient \( v_0 \) is assumed to change in an Arrhenius fashion

\[ v_0 = \text{const} \exp(-Q/RT) \] .......................... (A.2)
where $Q$ is the activation energy, $R$ is the gas constant, and $T$ is the temperature. This assumption also fits data well for temperature variations in glass subjected to water or water vapor [21].

Other investigators have derived relationships similar to (A.1), but through different means. For example, Liu [22] solved a steady-state stress-assisted diffusion equation to obtain the concentration of a degrading solute of the form

$$C = C_0 \exp(\beta \sigma) \ldots \ldots \ldots \ldots \ldots (A.3)$$

where $\beta$ and $C_0$ are constants, and $\sigma$ the hydrostatic stress. He then proposed that crack velocity $a$ was proportional to $C$ thus obtaining a relationship similar in form to (A.1).

Gerberich et al. [23] proposed a relationship similar to (A.1) for hydrogen assisted cracking by using a concentration solution like (A.3). They then incorporated into this relationship terms related to grain and plastic zone size. Puls et al. [24] proposed a model of crack growth due to the diffusion of point defects. This model might pertain to stress corrosion cracking.

Oriani [25] proposed a decohesion model of hydrogen embrittlement, based on ideas due to Troiano [8,26] that cohesive forces between atoms are reduced by hydrogen.
Oriani and Josephic [9] proposed that the cohesive force $\sigma_c$ is reduced by linearly

$$\sigma_c = \text{constant} - C_0 \exp(\beta \sigma) \ldots \ldots \ldots \ldots (A.4)$$

where $C_0$ and $\beta$ are constants. They then applied this relationship to threshold data for AISI 4340 steel subjected to hydrogen gas.

Rice [27] provided a thermodynamic foundation for stress corrosion cracking, but made no attempt to quantify crack growth rates.

In general, a relationship like (A.1) will model steady-state environmental cracking data if stage II and stage III growth are absent. Various glasses subjected to water have this characteristics, but many other materials do not.

Krausz [28] and Brown [29] proposed theories employing systems of parallel and series rate relationships of the form (A.1). It was shown that individual relationships of this type could be combined together to curve fit all three stages of steady-state crack growth.

In [30], Cherepanov proposed a simple steady-state model of continuous crack growth based on the diffusion of hydrogen. He assumed a constant flux of protons located at the crack tip. Unlike previous models, this model was truly steady-state and not quasi-static. Cherepanov also
proposed a quasi-static incremental model [30] based on the diffusion of hydrogen. Crack propagation was assumed to initiate when a critical concentration of hydrogen was reached.

Leeuwen [31] proposed a different quasi-static model of incremental crack growth where stress gradients were included in the diffusion equation. An approximate solution was obtained.

Unger and Aifantis [32] proposed a model applicable to hydrogen assisted crack propagation based on an equilibrium solution of a stress-assisted diffusion equation. Power laws between crack velocity and stress intensity factors were predicted of the form

\[ \dot{a} = v_0 K_1^n \] (A.5)

where \( n \) is the ratio of two diffusion parameters and \( v_0 \) is a constant.

In [10] and [11], Neimitz and Aifantis proposed an incremental model of hydrogen assisted cracking with crack opening displacement as a damage criterion.
APPENDIX C
CRACK OPENING DISPLACEMENT

In this appendix we will derive the crack opening displacement for the case of a constant cohesive force. This calculation is used in Eqs. (II.3) and (II.7).

The Barenblatt condition for an infinite plate is obtained from Eqs. (I.1), (I.2), and (I.3) as

\[ \sigma_0 \left( \frac{\pi c}{\gamma} \right)^{1/2} = 2 \left( \frac{c}{\pi} \right)^{1/2} \int_0^c \frac{\sigma_0}{(c^2 - x^2)^{1/2}} \, dx \quad \cdots \cdots \ (C.1) \]

For a constant cohesive force \( \sigma_c \), Eq. (C.1) may be readily integrated to yield

\[ \frac{a}{c} = \cos \left( \frac{\pi}{2} \left( \frac{\sigma_0}{\sigma_c} \right) \right) \quad \cdots \cdots \cdots \cdots \ (C.2) \]

This relationship will be used later.

The corresponding crack opening displacement for an infinite plate is given by Eqs. (II.1) and (II.2) as

\[ \delta = -\Lambda \int_a^c \frac{x}{(x^2 - a^2)^{1/2}} \int_a^x \frac{\sigma_0}{(x^2 - \xi^2)^{1/2}} \, d\xi \, dx + \]

\[ \Lambda (\pi/2) \sigma_0 \left( c^2 - a^2 \right)^{1/2} \quad \cdots \cdots \cdots \cdots \ (C.3) \]
For a constant cohesive force, the inner integration yields

\[ \delta = - \Lambda \sigma_c \int \frac{x}{(x^a - a^a)^{1/a}} \arccos\left(\frac{a}{x}\right) \, dx + \]

\[ \Lambda \left(\frac{\pi}{2}\right) \sigma_\infty (c^a - a^a)^{1/a} \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (C.4) \]

Now the integral in Eq. (C.4) is not commonly tabulated. However the powerful computer program MACSYMA (trademark of Symbolics, Inc.) gives the evaluation as

\[ \delta = \Lambda \sigma_c \left[ a \ln\left(\frac{c}{a}\right) - (c^a - a^a)^{1/a} \arccos\left(\frac{a}{c}\right) \right] + \]

\[ \Lambda \left(\frac{\pi}{2}\right) \sigma_\infty (c^a - a^a)^{1/a} \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (C.5) \]

If we now substitute Eq. (C.2) into Eq. (C.5) we find that Eq. (C.5) has reduced to the following

\[ \delta = \Lambda \sigma_c \left[ a \ln \sec\left(\frac{\pi}{2}\right) (\sigma_\infty / \sigma_c) \right] \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (C.6) \]

For \( \delta_\infty \ll \delta_c \), the first term of a Taylor series expansion is sufficient to represent Eq. (C.6). We find

\[ \delta = \Lambda \pi^a \sigma_\infty^a a / (8 \sigma_c) \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (C.7) \]

If \( c \) is small compared to \( a \) then Eq. (C.7) can be approximated by
\[ \delta = \frac{\wedge K_s^*}{(B \sigma_c)} \quad (C.8) \]
APPENDIX D

COMPUTER CODE FOR ANALYSIS OF
HYDROGEN ASSISTED CRACK PROPAGATION

C MAIN PROGRAM

C

IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION S(20),F(20),CTOD(200),A(200),DC(200),
ISIF(200),DB(20),B(10),AA(200),VEL(200),TX(200),
2T(10),D(20)

C

COMMON/ONE/N1,M1,NM1
COMMON/TWO/SIGMA, PI, C, COHF, GAMMA, RO, T
COMMON/THREE/E, SIGMAY, PMYU, A, AA, D, F
COMMON/FOUR/DCOF, Q, R, TEMP, ERROR

C INPUT
DO 10 I=1,10
READ(6,20) D(I),S(I)
20 FORMAT(2E13.6)
10 CONTINUE

C D(I) ARE THE GAUSSIAN WEIGHTS OF ORDER 2n,

C F(I) ARE DEFINED AS (1-S(I)*S(I)) WHERE S(I) ARE THE

C POSITIVE ZEROS OF LEGENDRE POLYNOMIAL P(2n)(X).
READ(5,30) E,PMYU,KIC,SIGMA,SIGMAY

30 FORMAT(5E13.6)

C
C E IS THE YOUNG'S MODULUS FOR THE MATERIAL.
C PMYU IS THE POISSON'S RATIO.
C KIC IS THE PLANE STRAIN FRACTURE TOUGHNESS.
C SIGMA IS THE APPLIED EXTERNAL STRESS.
C SIGMAY IS THE YIELD STRENGTH OF THE MATERIAL.
C

READ(5,40) DCOF,Q,TEMP,R

40 FORMAT(4E13.6)

C
C DCOF IS THE PRE-EXPONENTIAL FACTOR IN DIFFUSIVITY, D..Q IS THE ACTIVATION ENERGY, AND MAY BE ASSUMED AS A
C FUNCTION OF STRESS INTENSITY FACTOR.
C TEMP IS THE TEMPERATURE.
C R IS THE GAS CONSTANT.
C

PI=3.1415926D0
ERROR=1.D-03
C ERROR IS THE ERROR BOUND.
C
C COHF=SIGMAY
C COHF IS THE SigmaCo ; IT IS ASSUMED EQUAL TO
C SIGMAY(YIELD STRESS).
C
A(1)=0.4DO

AA(1)=A(1)

A(I) AND AA(I) ARE THE CRACK LENGTHS AT EACH STEP.

GAMMA=SIGMAY

GAMMA REPRESENTS THE COEFFICIENT WHICH RELATES THE
COHESIVE FORCE TO THE CONCENTRATION I. E. GammaC.

EPS=1.5D-03

EPS IS THE CONSTANT IN THE GammaCo DISTRIBUTION RO; DEFINED LATER

SIF(1)=SIGMA*DSQRT(PI*A(1))

SIF(I) EQUALS STRESS INTENSITY FACTOR.

DELC=(1.DO-PMYU*PMYU)*K1C*K1C/(E*SIGMAY)

DELC IS THE CRITICAL CRACK TIP OPENING DISPLACEMENT
OBTAINED FROM LINEAR ELASTIC FRACTURE MECHANICS.

WRITE(6,80) DELC

80 FORMAT(//'DELCC=',E13.6,//)

X=1.D-03

X IS AN INITIAL GUESS IN NEWTON'S ROOT FINDING SCHEME.

DO 100 I=1,100
II=II+1

R0=0.75D0-0.3D0/PI*DATAN(EPS*(SIF(I)-0.33D05))

C R0 IS GammaC, WHICH IS AN ASSUMED
C FUNCTION OF CRACK LENGTH.

C DO 300 J=1,2
      JJ=J+1
      JJJ=JJ+1
      IF(J .GE. 2) GO TO 110
      C FOR J=1 THE LOOP CALCULATES TIMES FOR THE CRACK
      C OPENING DISPLACEMENT TO REACH DELC.
      C FOR J=2 THE LOOP CALCULATES CRACK INCREASE BY SMALL
      C INCREMENTS, THUS REDUCING COD FROM THE CRITICAL
      C VALUE(DELC) TO THE ARREST VALUE, SETTING THE TIME
      C TO T=T(DELC).
      C
      T(J)=0. DO
      C INITIAL TIME

      260 T(JJ)=T(J)+1.D01
      C TIME INCREMENT IS 10 SECONDS.
      C
      CALL CODDY(I,CTOD,X,DC,I,JJ)
      C
      C CRACK TIP OPENING DISPLACEMENT(DC) IS NOW DETERMINED
      C GIVEN THE CRACK LENGTH A(I) AND TIME T(JJ).
DB(JJ) = DC(I) - DELC

CHECK WHETHER THE CRACK TIP OPENING DISPLACEMENT AT A
GIVEN TIME IS SMALLER THAN THE CRITICAL CRACK TIP
OPENING DISPLACEMENT.

IF (DB(JJ)) 250, 280, 280

IF THE CRACK TIP OPENING DISPLACEMENT IS SMALLER THAN
DELC, THEN INCREASE THE TIME.

HOWEVER, IF IT IS GREATER THAN DELC,
THEN FIND A REASONABLY ACCURATE TIME FOR
DC TO REACH DELC WITH THE GIVEN ERROR BOUND.

280 B(JJ) = (T(JJ) + T(J))/2.
DO
T(JJJ) = B(JJ)
CALL CODDY(I, CTOD, X, DC, I, JJJ)

CALCULATE DC AT A GIVEN TIME T.

DT = (DC(I) - DELC)/DELC
IF (DABS(DT) .LE. ERROR) GO TO 270

CHECK WHETHER THE DIFFERENCE BETWEEN DC AND DELC IS
WITHIN THE GIVEN ERROR BOUND.

IF NOT, CHECK WHETHER DC IS SMALLER THAN OR GREATER
THAN DELC AND FOLLOW THE SAME PROCEDURE AS BEFORE.

GO TO 290
250 T(J)=T(JJ)
GO TO 260

C

290 DB(JJJ)=DC(I)-DELC
IF(DB(JJJ)) 320, 330, 330
330 T(JJ)=T(JJJ)
GO TO 280

C WHEN DC IS GREATER THAN DELC, REPLACE T(JJ) BY
C T(JJJ).
C

320 T(J)=T(JJJ)
GO TO 280

C THIS IS FOR THE CASE FOR DC SMALLER THAN DELC.
C

270 CONTINUE
C WHEN DC IS REASONABLY CLOSE TO DELC DEFINE
C ALL THE VARIABLES.
    TX(II)=T(JJJ)
C TX STANDS FOR THE TIME TO REACH CRITICAL CRACK TIP
C OPENING DISPLACEMENT, DELC.
C
    T(J)=TX(II)
GO TO 300
C

110 A(J-1)=AA(I)
    CALL CODDY(J-1,CTOD,X,DC,I,J-1)
A(J) = A(J-1) + 1.D-03

INCREASE THE CRACK LENGTH BY 1.D-03 INCREMENTALLY.

CALL CODDY(J, CTOD, X, DC, I, J-1)

DC(J-1) = DC(J)
A(J-1) = A(J)

190 DDY = DC(J-1)

A(J) = A(J-1) + 1.D-03
CALL CODDY(J, CTOD, X, DC, I, J-1)
DDZ = DC(J)
DZY = DDZ - DDY

THE FOLLOWING STEP DETERMINES THE LOWER BOUND BY CHECKING FOR AN INCREASE IN DC WITH CRACK LENGTH.

IF(DZY) 910, 920, 920

910 A(JJ) = A(J) + 1.D-03
CALL CODDY(JJ, CTOD, X, DC, I, J-1)
DDW = DC(JJ)
DWZ = DDW - DDZ
IF(DWZ) 500, 510, 510

500 DC(J-1) = DC(J)
A(J-1) = A(J)
GO TO 190
510 DEL1=DDZ
  DDY=DC(J-1)
  DDW=DC(JJ)
  A(JJJ)=(A(J-1)+A(JJ))/2.DO
  CALL CODDY(JJJ,CTOD,X,DC,I,J-1)
  DDQ=DC(JJJ)
  DEL2=DDQ
  DELJ=(DEL1-DEL2)/DEL2
C FIND THE LOWEST VALUE IN DC BY ADJUSTING CRACK
C LENGTH AT THE GIVEN TIME.
  IF(DABS(DELJ) .LE. ERROR) GO TO 520
  DYW=DDY-DDW
  IF(DYW) 980,980,990
990 DC(J-1)=DDQ
  A(J-1)=A(JJ)
  GO TO 510
980 DC(JJ)=DDQ
  A(JJ)=A(JJJ)
  GO TO 510
920 DDY=DC(J-1)
  DDZ=DC(J)
  A(JJ)=(A(J)+A(J-1))/2.DO
  CALL CODDY(JJ,CTOD,X,DC,I,J-1)
  DDP=DC(JJ)
  DELJ=(DDP-DDY)/DDP
C FIND THE LOWEST POINT IN DC BY ADJUSTING CRACK
LENGTH AT THE GIVEN TIME.

IF(DABS(DELJ) .LE. ERROR) GO TO 380

DZY=DDZ-DDY

IF(DZY) 930, 930, 940

930 A(J-1)=A(JJ)

DC(J-1)=DDP

GO TO 920

940 A(J)=A(JJ)

DC(J)=DDP

GO TO 920

380 CONTINUE

AA(II)=A(JJ)

A(II)=AA(II)

DC(II)=DC(JJ)

CTOD(II)=CTOD(JJ)

GO TO 340

520 CONTINUE

AA(II)=A(JJJ)

A(II)=AA(II)

DC(II)=DC(JJJ)

CTOD(II)=CTOD(JJJ)

GO TO 340

300 CONTINUE

340 CONTINUE

WRITE(6,530) II,TX(II),X

530 FORMAT(/,10X,'II=',IS,10X,'TX=',}
C X REPRESENT THE COHESIVE ZONE LENGTH.
WRITE(6,620) II, AA(II), DC(II), CTOD(II)

620 FORMAT(//,10X,'II=',I5,10X,'AA=',E13.6,10X,'DC=',
       1E13.6,10X,'CTOD=',E13.6,}//)

SIF(II)=SIGMA*DSQRT(PI*AA(II)+X))
VEL(II)=(AA(II)-AA(II-1))/TX(II)
WRITE(6,650) II, SIF(II), VEL(II)

650 FORMAT(//,10X,'II=',I5,10X,'SIF=',E13.6,10X,'VEL=',
       1E13.6,}//)

100 CONTINUE
STOP
END

C
C SUBROUTINE CODDY CALCULATES CRACK OPENING
C DISPLACEMENT(DC) AT CRACK TIP.
C
C SUBROUTINE CODDY(N,CTOD,X,DC,NM,KK)
IMPLICIT REAL*8 (A-H,O-Z)
EXTERNAL QQ

C

DIMENSION A(200), D(20), P(20), DC(200), T(10),
IB(10), CTOD(200), AA(200)

C
COMMON/ONE/N1, M1, NM1
COMMON/TWO/SIGMA, PI, C, COHF, GAMMA, RO, T
COMMA/THREE/E, SIGMAY, PMYU, A, AA, D, F
COMMON/FOUR/DCOF, Q, R, TEMP, ERROR

DSY = 1. DO / DCOS(PI * SIGMA / 2. DO * SIGMAY)
CTOD(N) = 8. DO * (1. DO - PMYU * PMYU) * SIGMAY * A(N) / (E * PI) * 1DLOG(DSY)

CTOD IS THE LOWER BOUND OF CRACK TIP OPENING DISPLACEMENT, AND AFTER THE CRACK LENGTH IS DETERMINED, THIS VALUE IS CALCULATED AUTOMATICALLY.

C
C = 2. DO * DSQRT(DCOF * DEXP(-Q / (R * TEMP)) * T(KK))

DO 30 I = 1, 100
X1 = X

C INITIAL VALUE
GGINT = 0. DO
DGAINT = 0. DO
DGBINT = 0. DO

C THE BARENBLATT CONDITION IS USED TO OBTAIN COHESIVE ZONE LENGTH. AS THE EQUATION CONTAINS AN INTEGRAL WHICH HAS A SINGULARITY, A SPECIAL GAUSSIAN INTEGRATION SCHEME IS USED. TEN TERMS ARE EMPLOYED.

C
DO 40 L = 1, 10
FF = (A(N) + X*F(L) - AA(N))/C

XF = X*(1.0 + F(L))/2.0 + 2.0*A(N)

GG = D(L)*DERF(FF)/DSQRT(XF)

DGA = 0.5D0/DSQRT(X)*GG

FX = FF*FF

IF (DABS(FF) .GE. 1.0D0) GO TO 110

CAVOIDS A POSSIBLE UNDERFLOW.

GO TO 180

C

120 DGB = DSQRT(X)*D(L)*CS/(2.0*XF*DSQRT(XF))

GO TO 130

110 AS = 0.0D0

GO TO 200

180 AS = 4.0D0/(C*DSQRT(PI))*F(L)*DEXP(-FX)*XF

GO TO 220

200 BS = 1.0D0+F(L)

C

ALTHOUGH BS = DERF(FF)*(1.0 + F(L)), BS COULD BE

C

CONSIDERED TO BE (1.0 + F(L)), SINCE DERF(FF)

C

APPROXIMATELY 1 AS FF BECOMES GREATER THAN 10.

C

GO TO 210

220 BS = DERF(FF)*(1.0 + F(L))

210 CS = AS - BS

IF (DABS(CS) .LE. 1.0D-10) GO TO 190

GO TO 120

190 CS = 0.0D0
C THIS STATEMENT IS USED TO AVOID AN UNDERFLOW.
GO TO 120
130 CONTINUE
C THE FOLLOWING PROCEDURE ADDS THE TERMS.
C
GGINT=GGINT+GG
DGAINT=DGAINT+DGA
DGBINT=DGBINT+DGB
40 CONTINUE
C THE PRECEDING STEPS APPLY THE GAUSSIAN INTEGRATION
C SCHEME. FOLLOWING STEP IS USED TO FIND THE ROOT
C IN THE BARENBLATT CONDITION BY NEWTON METHOD.
C
H=(COHF-GAMMA*RO)*(PI/2.DO-DASIN(A(N)/(A(N)+X)))
C
U=SIGMA*PI/2.DO
C
V=H+2.DO*GAMMA*RO*DSQRT(X)*GGINT-U
C
DH=(COHF-GAMMA*RO)*A(N)/(A(N)+X)*DSQRT(X*(2.DO*A(N)+1X)))
C
DV=DH+2.DO*GAMMA*RO*(DGAINT+DGBINT)
C
X=X-V/DV
C
X2 = X
DX = (X1 - X2) / X1
IF (DABS (DX) .LE. ERROR) GO TO 50

C CONVERGENCE CRITERION CHECKED.

30 CONTINUE
50 X = X2
    FA = X
    CA = A(N)
    GA = FA + CA

C

C FOLLOWING STEP IS TO ADD THE REMAINING TERMS FOR DC. DURING THE PROCESS, CERTAIN TERMS ARE CANCELLED BY BARENBLATT CONDITION.
    TFINT = 0.
    DO 60 L = 1, 10
      GF = CA * (1. DO - F(L)) + GA * (1. DO + F(L))
      TF = D(L) * DERF ((GF - GA - AA(NM)) / C) / DSQRT(GF)
      TFINT = TFINT + TF
    60 CONTINUE

C

C TW = 2. DO * GAMMA * RO * (GA - CA) * DSQRT(GA + CA) * TFINT

C

C TY = (COHF - GAMMA * RO) * CA * DLOG(CA / GA)

C

C FOLLOWING STEP IS TO CARRY OUT DOUBLE INTEGRATION BY GAUSSIAN QUADRATURE AND THEN INTEGRATED BY IMSL
C SUBROUTINE DCADRE TO AVOID THE USE OF A RECURSIVE
C SUBROUTINE.

NM1=NM
N1=N
M1=M
DA=CA
HA=GA
AERR=1.D-10
RERR=1.D-10

CF=GAMMA*RQ*DCADRE(QQ,DA,HA,AERR,RERR,ERROR,IER)

DC(N) = 4.DO*(1.DO-PMYU)/PI*(TW-TY-CF)

DC IS THE FINAL VALUE FOR THE CRACK TIP OPENING
C DISPLACEMENT AT A GIVEN TIME AND CRACK LENGTH.

RETURN
END

C

FUNCTION QQ(TT)
C FUNCTION QQ IS THE INTEGRAND FOR USE
C BY IMSL DCADRE.
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION D(20),F(20),A(200),B(10),AA(200),T(10)
C

COMMON/ONE/N1, M1, NM1
COMMON/TWO/SIGMA, PI, C, COHF, GAMMA, RO, T
COMMON/THREE/E, SIGMAY, PMYU, A, AA, D, F
COMMON/FOUR/DCOF, Q, R, TEMP, ERROR

C

QCINT=0.DO
DO 20 L=1,10
QA=(A(N1)*(1.DO-F(L))+F(L)*TT-AA(NM1))/C

C

QB=A(N1)*(1.DO-F(L))+TT*(1.DO+F(L))

C

QC=D(L)*DERF(QA)/DSQRT(QB)

C

QCINT=QCINT+QC
20 CONTINUE

C

QQ=2.DO*TT/DSQRT(TT+A(N1))*QCINT

C

RETURN

END