MCC**Materials Characterization Center****Assessment of Predictive
Models for the Failure of
Titanium and Ferrous Alloys
Due to Hydrogen Effects**

April 1982**Prepared for the U.S. Department of Energy
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Materials Characterization Center

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**Report for the Period of
June 16 to September 15, 1981**

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CONTENTS

	<u>Page</u>
PURPOSE AND SCOPE OF STUDY	1
ASSESSMENT OF RECENT LITERATURE RELATED TO HYDROGEN INDUCED DELAYED FRACTURE IN TITANIUM AND IRON-BASE ALLOYS	3
Introduction	3
Hydrogen Embrittlement Models	3
Diffusion Modelling of Crack Growth	8
Hydride Forming Metals--Hydrogen Flux	8
Hydride Forming Metals--Crack Growth	17
Non-Hydride Forming Metals--Crack Growth	22
Summary of Phenomenological Crack Growth Models	24
RELEVANT FRACTURE TOUGHNESS TESTS	33
Introduction	33
Crack Growth Measurements and the Threshold Stress Intensity K_{Th}	34
Plane Strain vs. Elastic/Plastic Failure Conditions	40
Recommended Predictive Test For Plane Strain Conditions	45
CONCLUSIONS AND RECOMMENDATIONS	48
REFERENCES	51
TABLES	58
APPENDIX: LITERATURE SUMMARIES, CRACK GROWTH AND CRACK GROWTH RATES	A-1

PURPOSE AND SCOPE OF STUDY

A critical assessment of the literature has been undertaken to determine the relevance and reliability of existing theoretical models and test methods for predicting the initiation and subcritical growth of cracks leading to fracture over prolonged periods under stress and in the presence of various chemical environments, especially those containing hydrogen. The evaluation of recent crack growth models for describing hydrogen-induced fracture is an important first step in establishing a confident basis for predicting the resistance to delayed failure of titanium and iron-base alloys from the results of relatively short time tests. The conditions for hydrogen embrittlement in these two classes of materials are quite different since delayed fracture in titanium alloys depends on hydride formation and fracture at the tips of pre-existing flaws or cracks; whereas, iron-base alloys do not undergo hydride formation. The applicability of existing diffusion models for hydrogen embrittlement and the available test methods of fracture mechanics to these two conditions of hydrogen embrittlement has been a major concern of this present study.

The following specific topics have been considered within the purpose and scope of the assessment study.

1. Critical assessment of the validity of crack growth rate calculations based on recent models proposed for hydride-forming materials, including the expected complications due to environmental and microstructural considerations.

2. Determination of the data required for the confident application of crack growth models in predicting the conditions for delayed fracture and crack growth rates.
3. Evaluation of available testing methods, and especially their potential usefulness for assessing the performance of titanium and ferrous alloys with respect to delayed failure over prolonged time periods for the conditions of stress and chemical environment expected under nuclear waste containment conditions.
4. Assessment of the environmental parameters expected to influence the evaluation or calculation of growth rates from theoretical models; specific parameters include H_2 solubility, stress and temperature, all of which are important considerations with respect to nuclear waste canisters.

ASSESSMENT OF RECENT LITERATURE RELATED TO HYDROGEN INDUCED DELAYED FRACTURE IN TITANIUM AND IRON-BASE ALLOYS

Introduction

The available literature records numerous investigations of the influence of hydrogen on the mechanical properties of metals; several embrittlement mechanisms have been proposed, each of which is applicable to only a limited variety of materials and only a portion of the published data. As indicated by Louthan and McNitt (1), "...a review of the literature shows that all too often experiments are designed to infer weaknesses in one or more theories without providing solid support for any proposal." This view is shared, in general, by the present authors who have attempted to conduct a critical assessment of the recent literature related to hydrogen embrittlement models, crack growth kinetics, and predictive test methods for the evaluation of the crack growth resistance of metals over prolonged periods of time.

Hydrogen Embrittlement Model

Several major embrittlement mechanisms have been proposed to account for the effects of hydrogen in promoting the initiation or propagation of fracture in metals and alloys. These mechanisms include the following:

1. Internal pressure theory: This model proposed originally by Zapffe (2) requires hydrogen to enter the material and to build up pressure in internal voids or defects. According to this model which has been modified by several investigators (3-6),

the apparent fracture stress is reduced due to the combined effects of applied stress and the internal pressure developed by hydrogen at internal defects.

2. Troiano model (7): According to this model, hydrogen in solid solution reduces the cohesive strength of the lattice, thereby reducing the fracture strength and causing brittle behavior; Oriani (8) has modified this model.
3. Petch and Stables (9): This theory proposed that hydrogen is absorbed at the crack tip thereby leading to a reduction in the surface energy required for crack formation and modifying the Griffith condition for crack extension; the mechanism, first proposed by Petch and Stables, has been modified by several recent workers (10-11).
4. Dislocation model due to Beachem (12,13): It has been proposed that hydrogen absorption can increase both dislocation motion and the generation of dislocations. This model differs from other proposals in that crack tip plasticity is enhanced by the entry of hydrogen into the matrix, and the resulting plastic deformation aids the entry of hydrogen into the critical crack tip region.
5. Formation of hydrogen-rich phases (e.g. hydrides) (14): Embrittlement is associated with the formation and fracture of hydride particles nucleated at the region of stress intensification immediately adjacent to the crack tip. The fracture process is generally viewed as discontinuous since the mechanism depends on the diffusion of hydrogen followed by hydrogen-

rich precipitate formation, crack movement, precipitate redissolution, and redistribution of the hydrogen to the region ahead of the advancing crack to repeat the sequence.

6. Hydrogen-dislocation interactions (15-19): Although not included as a general embrittlement mechanism by many investigators, the association between hydrogen atoms and dislocations has been considered as a contributing factor to lattice embrittlement by restricting the movement of dislocations or providing an opportunity for localized hydrogen enrichment.

The original theory proposed by Zapffe (2) requires internal pressure to act as a driving force for fracture after hydrogen has entered a metal and diffused some distance beneath the surface, thereby creating subsurface voids and openings. According to this model, repetitive subsurface nucleation is expected to leave evidence of discontinuous crack growth on the fracture surface. This theory was modified by Tetelman (5) who concluded that the interfaces between nonmetallic inclusions and the metal matrix of various alloys provide favorable sites for the accumulation of hydrogen gas under high pressures. It has been further argued that such gas pressure accumulation can cause material failure even in the absence of an applied stress (20), except in those cases where the fracture mode involves microvoid coalescence. There has been limited fractographic evidence of discontinuous cracking as a result of cleavage and intergranular failure mechanisms. For this reason, plus the argument that hydrogen-induced failure occurs under conditions of low external hydrogen pressure, the pressure theory of embrittlement has

received less attention in the recent literature as a plausible mechanism.

The lattice embrittlement theory, proposed originally by Troiano (7) and modified later by Oriani (8), can be applied to both continuous and discontinuous cracking on both the macroscopic and microscopic scales. This model is also independent of whether the hydrogen is present in the material prior to the application of stress or whether it is introduced from the environment at a growing crack tip. The decohesion theory requires non-deformation atomic separation processes to occur; such a mechanism cannot be directly observed and must be inferred from observations of reduced ductility and the predominance of cleavage and intergranular fracture that is characteristic of many hydrogen-assisted cracking failures. A major disadvantage of the Troiano and Oriani models is the failure to account for the plasticity frequently observed on the fracture surface after hydrogen-induced failure. It can be argued, however, that decohesion leads to the initiation of fracture by the formation of microvoids and cracks between tear ridges prior to the occurrence of general failure due to overload.

The crack tip plasticity theory proposed by Beachem (12) does not depend upon continuous or discontinuous cracking as a mode of failure. Furthermore, it is not dependent on hydrogen being either inside or outside the matrix and does not require failure to occur by a classical cleavage process; it is therefore consistent with the usual observation of plasticity on the fracture surface of steels subjected to hydrogen-induced failure. A major weakness of the Beachem model is the fact that it does not account for the expansion or contraction of the matrix

lattice, nor does it directly address the role of hydrogen solubility, diffusion, or internal friction effects. Furthermore, the model has not been related to the velocity of crack propagation and in its present form is designed to apply specifically to iron-base alloys.

A number of recent investigations (21-30) described in an earlier report (31), together with important studies reported during the past year (32), associate the origins of delayed fracture in some materials with the diffusion of hydrogen to regions of high stress intensification and the subsequent precipitation of hydrides. These processes control hydrogen embrittlement and delayed fracture in a number of reactive metals that exhibit limited solubility for hydrogen and a strong tendency to form hydride compounds. Consequently, the fifth general mechanism described above provides an adequate description of the hydrogen embrittlement in a number of metals falling under the general category of hydride formers.

Experimental observations indicate that the mechanism of hydrogen-induced failure may vary for different materials and is dependent on a variety of parameters including hydrogen, pressure, temperature, microstructure, hydrogen solubility, compound-forming tendencies, and applied stress. It is apparent that no single mechanism or model can account for all of the hydrogen-assisted cracking phenomena observed in various metals and alloys. The factors influencing the kinetics of crack growth differ from one material to another, and any test methods developed to predict the resistance of materials to crack growth must necessarily account for environmental conditions as well as applying equally well to varying conditions of hydrogen interaction with the microstructure. The

latter may be in the form of increased local pressure at internal defects, atomic decohesion, or the precipitation of second phases such as hydride particles resulting from hydrogen enrichment at regions of stress intensification.

Diffusion Modelling of Crack Growth

Hydride-Forming Metals--Hydrogen Flux

There are several mathematical model developments that are related to the hydride formers. The models have been published within the last 10 years, and they will probably experience revisions over the coming years as experimental work progresses. Most efforts have been directed toward titanium and many of its alloys and toward the nuclear-related zirconium alloys.

A key step in the models is a necessary assumption that can relate the flux of hydrogen, and thus the rate with which hydrogen arrives at a growing hydride precipitate, to the rate of crack propagation; these assumptions are discussed later. The various internal and external factors that can affect the hydrogen flux have received the most attention; such factors include hydrogen content in the base metal, alloying content, hydrogen solubility, internal constraints, external stress, local temperature, and temperature gradients. The developed flux equations are described below in approximate order of increasing complexity, and they are identified arbitrarily by the authors' names which appear most frequently on the relevant papers; also, the authors' original notations and definitions are generally given.

A. Waisman-Sines-Robinson (25)

Their equation for the flux of hydrogen in titanium alloys was discussed in our earlier report of 9 September 1980, and is repeated here:

$$J = -D \left[\frac{dc}{dx} + 3.55c \frac{dN_a}{dx} - \frac{(5.5 \times 10^{-4})c}{T} \frac{d\sigma_{ii}}{dx} + \frac{c(2676 - 294N_a)}{T^2} \frac{dT}{dx} \right]$$

where J = hydrogen flux in (PPM) (CM/SEC)

c = hydrogen concentration in PPM

D = hydrogen diffusivity in (CM²/SEC)

x = distance in CM

N_a = atom fraction of aluminum

σ_{ii} = sum of principal stresses in PSI

T = degrees K

This empirical equation assumes that each of the gradients (aluminum content, stress, and temperature) contribute to the flux as a simple addition to or subtraction from the steady-state Fick's first equation for flux. Their equation was given as an example of the use of a more general equation; the constants were obtained from measurements of hydrogen gas pressures in equilibrium with various hydrogen contents in stressed CP Ti rods and Ti-6Al-4V tubing, assuming uniaxial stressing and for bodies with isotropic or cubic symmetry. Their general equation, for anisotropic symmetry is:

$$(J_m)_i = - \sum_{j=1}^3 D_{ij} C_m \left[\left(\frac{\partial \ln a_m}{\partial C_m} \frac{dC_m}{dx_j} \right)_T + \left(\frac{\partial \ln a_m}{\partial C_2} \frac{dC_2}{dx_j} \right)_T \right. \\ \left. - \frac{1}{RT} \left(\frac{d[-RT \ln a_m]}{dx_j} \right)_T + \frac{Q^*}{RT^2} \frac{dT}{dx_j} \right]$$

where $(J_m)_i$ = flux of mobile species m (hydrogen) in direction i

a_m = activity of mobile species

j = 1,2,3 refer to three orthogonal axes

$-RT \ln a_m$ = work done on the body per mole of addition of m by an arbitrary stress field

Q^* = heat of transport (thermal diffusion)

C_2 = concentration of stationary species 2 (e.g., aluminum)

The authors give a general equation for the variation of C_m with time (Fick's second equation), but do not give numerical examples. The predicted component of the flux due to spatial variations in the aluminum content would be negligible for homogeneous, single phase alloys, but the diffusivity of hydrogen must be expected to vary with solute content.

B. Simpson-Puls-Dutton (33-36)

The group at AECL has been concerned with hydrogen flux and crack growth rates in zirconium alloys. While acknowledging that the crack growth process often occurs in an intermittent fashion, their original formulation is for an average growth rate; this crack growth rate was

assumed to be determined by the rate of hydride growth. The model does not consider hydrogen sources or paths (e.g., external hydrogen, traps, etc.); it is based on a flux biased toward a growing hydride platelet as a result of hydrostatic stress differences. Hydride precipitates in lower (tension) stressed volumes (removed from the advancing crack tip) are assumed to dissolve and supply hydrogen to the growing hydride. Recently, vanadium hydride dissolution following the passage of a crack has been observed directly in the TEM work of Koike and Suzuki (32). The flux equation published in 1977 (35) and modified in 1979 (34) is for steady state diffusion with a terminal solubility of hydrogen in solution (at zero applied stress at a given temperature) being modified by terms incorporating the difference in hydrostatic stress (1977) or by terms incorporating elastic strain energy (matrix/hydride misfit) and interaction energy of a hydride with an applied stress field (1979).

The 1977 flux equation involves quantities which are in general more readily determined or estimated. It is assumed that all of the hydrogen entering a cylindrical region (centered on the crack tip) or 'sink' of radius ℓ precipitates at the existing, growing hydride; the radius ℓ corresponds to the center of the plastic zone and is defined as the distance from the location of the maximum stress to the crack tip. The flux equation is:

$$J_H = \frac{D_H C_H^S \exp(p(L) \bar{V}_H^h / RT)}{r \phi \Omega_{Zr}} \left[1 - \exp(\Delta p \bar{V}_H^h / RT) \right]$$

where D_H = hydrogen diffusivity in the matrix

C_H^S = terminal solubility of hydrogen in stress free state

$p(L)$ = local hydrostatic stress at distance L , remote from advancing crack tip; L , taken as the mean interhydride distance in the matrix, corresponds to a cylindrical 'source' of hydrogen

$p(\ell)$ = local hydrostatic stress at $\ell \approx -2.4 \times$ yield stress

$$\Delta p = p(\ell) - p(L)$$

$\bar{V}_H^h$ = molal volume of hydrogen in the hydride

Ω_{Zr} = atomic volume of Zr (or Ω_{Ti} , etc.) in the matrix

r = variable distance from crack tip

$$\Phi = \int_{\ell}^L r^{-1} \exp(\Phi(r)/RT) dr \approx \ln(L/\ell)$$

$$\Phi(r) = \frac{2(1+\nu)K_I \bar{V}_H}{3\sqrt{2\pi r}} + \frac{(1+2\nu^2)K_I^2 \bar{V}_H}{2\pi r E}$$

= interaction energy of hydrogen in solution with local stress field

$\bar{V}_H$ = molal volume of hydrogen in the matrix

The model for the crack velocity was modified (36) with the hypothesis of a critical crack length, ℓ_c , which was based on crack arrest fronts (striations) observed on fractographs. The crack-advance step (striation spacing) is taken as the critical hydride length and was found to increase with temperature.

The flux equation was modified further in 1979 following more detailed observations of crack growth in Zr-2.5 Nb to:

$$J_H = \frac{D_H C_H^S}{r \phi \Omega_{Zr}} \left\{ \exp[\bar{w}_t^{inc}(L)/RT] \exp[\bar{w}_t^a(L)/RT] \right. \\ \left. - \exp[\bar{w}_t^{inc}(\ell)/RT] \exp[\bar{w}_t^a(\ell)/RT] \right\}$$

where $\bar{w}_t^{inc}$ = total molal elastic strain energy of the matrix and the hydride; positive in tension

$\bar{w}_t^a$ = molal interaction energy of a hydride with an applied elastic field, analogous to the previous pV_H^h terms; negative in tension

The authors assumed, for purposes of their calculations, that the elastic constants of the hydride and of the matrix are equal in order to evaluate $\bar{w}_t^{inc}$; their numerical analysis of the available data shows that the only significant change from the earlier flux equation appears in the $\bar{w}_t^{inc}$ terms. These terms do not depend on applied stress but rather on the degree of misfit accommodated by elastic deformations; the calculated values of $\bar{w}_t^{inc}$ were reported for several precipitate morphologies and orientations, with the plate precipitates having their plate normals parallel to $\langle 0001 \rangle$ being the most prevalent.

It is not clear from the published information and data that the numerical values for the flux of hydrogen, as calculated from the 1977 or 1979 versions are significantly different for the zirconium alloy. In both models the stress free solubilities are modified by the exponential terms, in accord with the observed appearance of hydrides in stressed material whose hydrogen content would normally not be adequate for isothermal, external stress-free precipitation; no consideration is given to the probability that the stress-free diffusivity, D_H , is altered in a stress field.

The authors believe that the elastic constraints play a significant role in controlling the rate of hydrogen transport, and that the driving force is the increased tensile stress at the crack tip.

C. Pardee-Paton (37)

A much more detailed model for the flux of hydrogen and for sustained load cracking in titanium alloys is presented. The overall form of the analysis is similar to that of Simpson-Puls-Dutton. The mathematically more complex treatment by Pardee and Paton arises because of the description of anisotropic, two-dimensional, time dependent hydrogen diffusion near a crack tip and because of the relationship between the diffusion and a model for hydrogen solubility in an elastoplastic strain field.

The model for hydrogen diffusion near the crack tip (taken to be under plain strain conditions) necessitates the introduction of a 'hydrogen pseudo-density' (spatially varying concentration) and a pseudo-diffusion coefficient in order to circumvent a mathematical difficulty: derivatives becoming singular at the elastic-plastic transition.

The hydrogen solubility in a strain field is taken as the concentration at which hydride begins to form, which in turn is determined by equating the chemical potential of hydrogen in solution to that of hydrogen in the hydride. The formation of titanium hydride, which has a molar volume approximately 18% larger than the matrix, requires both elastic and plastic work on the matrix. Zirconium hydride exhibits a 14-17% volume expansion by comparison. The presence of a crack will decrease the solubility because its stress field can provide part of the required work. The authors state that the solubility shift portion of

their model is "qualitatively reasonable and consistent"; many of the parameters, particularly the plastic work values, must be estimated.

D. Koike - Suzuki (32)

The direct observation of hydride behavior in vanadium was done with an HVEM equipped with a tensile stage, and the authors reported two types of crack behavior:

Type 1: Intermittent cracking at an applied stress less than a critical stress σ_c . The critical stress is determined by a resistive force, due to the presence of an atmosphere of hydrogen atoms in front of the crack, which suppresses the continuous advance of the crack. In spite of the resistive force, hydrides may be formed and cracks nucleated, but only in an intermittent fashion; the hydrides are believed to form by a phase decomposition similar to a spinodal decomposition in a homogeneous system.

Type 2: At an applied stress greater than σ_c , the crack propagates almost continuously, via hydride cracking, to the extremity of the hydrogen atmosphere. The atmosphere then reforms around the new crack tip position. Smaller hydride precipitates are observed in this regime.

The Type 1 and Type 2 crack behavior reported by the authors are analogous to the Stage I and Stage II behavior seen on plots of crack velocity vs. stress intensity K . The authors do not give a detailed flux equation for their Type 1, but for Type 2:

$$J_2 = -(DA/kT)(2c_\beta R^{\frac{1}{2}})$$

where $A = \frac{4\pi}{c} \frac{\Delta a}{a} \left(\frac{1-\nu}{1+\nu} \right) K$

c = volume concentration of H atoms

ν = Poisson's ratio

$\Delta a/a$ = fractional change in lattice parameter due to a hydrogen atom in an interstitial site

c_β = volume concentration of hydrogen in the hydride

R = variable radius of the hydrogen atmosphere; $c = c_\beta$ for radii less than R

The critical stress σ_c is not to be confused with or associated with a threshold K , but rather with a transition from Stage I to Stage II.

E. Pressouyre (38) "Trap Theory"

The theoretical work of Pressouyre is included here as it is related to hydrogen transport in both the hydride formers and the non-hydride forming metals. The premise of the theory is that both reversible and irreversible sites exist in metals; these sites either accept and give up hydrogen readily (reversible) or other types of sites (irreversible) tend to accumulate hydrogen. The specific character of a trap must be known, however, in order to apply the theory; that is, both the reversible and irreversible trap densities must be known or estimated. Examples of traps are grain boundaries, inclusions, and dislocations.

The theory seems to be capable of explaining the different embrittlement characteristics that often are observed for specimens containing internal hydrogen and specimens exposed to gaseous hydrogen.

As an example, Pressouyre cites two possible cases for the transport of hydrogen from an external source:

- a. If the initial concentration carried by moving dislocations is constant, all traps act as sinks, reversible traps fill quickly, and hydrogen penetrates deeply into the metal.

- b. If the initial concentration of hydrogen carried by dislocations is decreasing, the reversible traps act as sources, and a concentration maximum is predicted at some level below the surface.

If, on the other hand, the hydrogen is internal (precharged) all reversible traps act as sources of hydrogen and the effect varies with trap character and population.

The present theory does not yet appear to be suitable for application to a reliable predictive model.

Hydride-Forming Metals--Crack Growth

As stated earlier, a key step must be made to relate the hydrogen flux to an actual cracking process, and the models generally attempt to give a crack growth rate that can be compared with experimental data. This key step involves an assumption regarding the relationship between the rate of hydrogen transport, and thus the rate of hydride growth, and the rate of crack advance. The discontinuous or intermittent crack growth observed at low stress intensities has presented a problem to the modelers.

The Simpson-Puls-Dutton model addresses the problem directly by equating the observed 'striation' spacing seen on fracture surfaces to the intermittent growth steps. A mechanical model is used wherein the growing hydride at the crack tip is considered to be 'hinged' at the end away from the crack tip, experiencing a stress proportional to its length. At some critical length, the increasing moment leads to hydride

rupture. The number of hydrogen atoms per second arriving at a cylinder of radius r , along a unit length of crack, is given as:

$$\frac{dn}{dt} = 2\pi r J_H$$

Assuming that the crack grows at the same rate as the hydride (a major assumption in the analysis), the average crack velocity is:

$$v = \left[\frac{1}{\alpha \pi \ell_c C_c} \right] \frac{dn}{dt}$$

where ℓ_c = the critical hydride length for rupture, taken as the striation spacing

α = ratio of minor to major ellipse axes, assumed to be constant, related to the elliptically shaped plastic zone

C_c = the average local concentration of hydrogen in the form of hydride at rupture

By making a further assumption that the hydride MH_x grows with a thickness equal to twice the effective crack tip radius, the crack velocity reduces to:

$$v = \frac{\Omega_{\text{hydride}}}{x(2\ell^*)} \frac{dn}{dt}$$

where ℓ^* = the effective crack tip radius.

The velocity equation then becomes:

$$v = \frac{\pi \Omega_{\text{hydride}} (D_H C_H^S)}{x(\ell^*) \ln(L/\ell) \Omega_M} \exp \left| \begin{array}{l} \text{The stress or} \\ \text{energy terms} \end{array} \right|$$

The velocity result is for Stage II cracking which is relatively insensitive to the stress intensity; Simpson and Puls suggest that Stage I does not exist in carefully preconditioned cracks, at least in their Zr alloys.

The critical hydride length in the Simpson-Puls-Dutton model was assumed to be the observed striation spacing (stretch zones) which was found to vary strongly with temperature and weakly with stress intensity. Koike and Suzuki (32) in the vanadium hydride TEM work, observed similar 'steps' on the opening crack surface which they attribute to a temporary blunting caused by the formation of a hydride at the crack tip and subsequent joining of this area with isolated microcracks just in front of the major crack. The latter investigators also found that the location of the hydrides, on one or both sides of a major crack, was dependent on the specific loading direction in a given grain.

The utility of the Simpson-Puls-Dutton model is tempered with their own statement that "the criterion for the fracture of the crack-tip hydride is still not understood".

Pardee and Paton (37) make the step from flux to crack growth in the same way as Simpson-Puls-Dutton: the velocity is equated with the rate of hydride length increase. The use of their model requires "technically complicated techniques". They have shown that for Ti-Al alloys the model qualitatively predicts the observed maximum in velocity vs. temperature plots, but the quantitative results are not yet adequate. Also, the authors have predicted that the growth rate, at a constant temperature, is not constant for computations carried out to 10 hours; at 20°C, for example, the rate of growth in a 100 ppm hydrogen alpha titanium alloy is predicted to decrease and then to increase slowly with time.

The velocity equations given by Koike and Suzuki for their two types of cracking are:

$$v_1 = - \frac{3}{4} \frac{(DA)}{kT} (x_0)^{-3/2} \quad \text{and}$$

$$v_2 = - \frac{2}{\pi} \frac{(DA)}{kT} R^{-3/2}$$

where x_0 is apparently the 'step' or 'striation' spacing on the crack surface, and the other quantities were defined earlier. The authors show that their calculated values of v_1 are in reasonable agreement with experimental data.

Moody and Gerberich (22) found that microstructure has a strong influence on slow crack growth in the Ti-6Al-6V-2Sn alloy when examined in terms of an effective stress intensity, K_{eff} . The authors quantify the microstructural effect, which for their alloy was determined to reduce the stress intensity at the crack tip, and consequently modify the applied K to K_{eff} .

Moody and Gerberich developed a model for an effective stress intensity K , corresponding to incipient cracking or threshold. This model assumes that the strain induced hydrides form when the hydrogen concentration reaches the solubility limit. By equating these hydrogen concentrations and using mode I elastic stress solutions they give:

$$K_{eff} = [\ln (\alpha/C_0) - (\Delta G^\circ - W)/RT] \frac{3(2\pi r)^{\frac{1}{2}} RT}{4(1+\nu)\bar{V}_H}$$

where: α = a solubility constant determined from experiment

C_0 = the initial hydrogen content in the lattice

ΔG° = the standard free energy of hydride formation

W = molar strain energy

$\bar{V}_H$ = partial molar volume of hydrogen in the matrix

r = taken as the average grain size

In a more recent paper, Moody and Gerberich (39) use this expression in a slightly revised form to calculate K_{eff} for the Ti-6Al-6V-2Sn alloy; they conclude that the revisions, which relate to plastic work done by dislocations during hydride formation, have only a small effect on the resulting K_{eff} values. Of more concern, however, was their use of an enthalpy value for the free energy ΔG° ; a re-evaluation may alter their conclusion.

In summary, each of the models for predicting crack growth rates in the hydride-forming metals appear to suffer from some form of uncertainty. The 1977 version of the Simpson-Puls-Dutton model seems to be the most amenable with respect to the utilization of known or readily estimated quantities, but it, like the other models, is not capable of dealing with crack initiation or threshold conditions. The added complexities of the Pardee-Paton model do not offer advantages over the AECL work at this time; extensive calculations involving estimated quantities appear to be necessary, and the results achieved are only qualitatively correct in agreeing with experimental data. Both of the above models assume that the crack will grow at the same rate as the hydride. The sparse data presented by Koike and Suzuki in support of their hydrogen atmosphere--displacive transformation model needs to be expanded; their work was based on thin foil TEM work specimens, and they acknowledge in their paper that additional experiments would be necessary with bulk specimens.

Non Hydride Forming Metals--Crack Growth

Appendix I and Table I summarize the observations of a number of investigators (22, 30, 34, 40-48) relevant to hydrogen-induced slow crack growth as a function of applied stress intensity, hydrogen pressure, temperature, and strength level. The following general characteristics relate to the influence of hydrogen on the mechanical behavior of steels which are non-hydride formers:

- Exposure to hydrogen reduces the stress intensity for slow crack growth.
- There are at least three stages of growth, each having different dependencies of growth rate on the stress intensity.
- The influence of temperature and hydrogen pressure on crack growth rates differs for the different stages of growth.
- The fracture modes vary for different stages of growth.
- Crack growth in hydrogen may be modified at least to some extent by small quantities of oxygen and/or water vapor in the environment.
- Microstructural modifications due to alloy heat treatment as well as variations in hydrogen content will influence the critical stress intensity for slow crack growth.
- The size of the plastic zone in samples exposed to hydrogen is larger than for those exposed to air for a given stress intensity and specimen thickness.

From Appendix I and Table I it is apparent that relatively little attention has been devoted to the influence of microstructure on the threshold stress intensity and the processes of sub-critical crack

growth. Lessar and Gerberich (41) conclude that the crack growth kinetics in steels are diffusion limited and influenced by prior austenite grain size, which in turn has a mild effect on K_{Th} and K_{ISCC} values. Doig and Jones (42) reported observing discontinuous cracking following an incubation period; they concluded that crack initiation depended on a critical hydrogen concentration that must be achieved over an unspecified distance determined by the microstructure. In a recent paper, Akhurst and Baker (48) reported that cracks in steel advance by the repeated nucleation of microcracks just ahead of the main crack, and the discontinuous nature of the cracking rate was confirmed by acoustic emission techniques. These investigators reported that the crack path is often associated with prior gamma grain boundaries, inclusions, and lath boundaries. By employing a sensitive back face strain technique they were able to detect transient crack growth resulting from load increases just below K_{Th} . Akhurst and Baker also developed an equation relating the critical stress for fracture to hydrogen pressure; unfortunately, many of the parameters in the equation cannot be measured experimentally.

The observation of crack growth in steels under static load conditions indicates that crack movement is apparently discontinuous for constant hydrogen pressure (49-51). It has been shown that self-arrested cracks can tend to propagate by simply increasing the hydrogen pressure (52) and that a propagating crack subjected to a change in gas pressure will experience a change in crack growth rate under conditions of either sustained load or alternating loads. There is uncertainty among various investigators as to whether or not the discontinuities in crack growth

are inherently associated with hydrogen embrittlement and the extent to which microstructural parameters are involved.

Summary of Phenomenological Crack Growth Models

Considerable attention has been recently given (40,41,43,47) to the mathematical modeling of crack velocity in many structural materials. Most of these models describe crack growth rate (da/dt) in terms of stress intensity (K), grain size, temperature, and hydrogen diffusivity (D_A).

The most detailed treatment of crack growth rates (da/dt) is reported by Gerberich, Chen, and St. John (43), where models for (da/dt) are given for Stage I, II, and III cracking. Stage I cracking was found to be elastically controlled, with the crack velocity given by

$$\left(\frac{da}{dt} \right)_I = \frac{2(1+\nu) C_0 D_A \bar{V}_H K}{3d^{3/2} RT (C_{cr} - C_0)} \quad (1)$$

where ν = Poisson's Ratio

C_0 = initial hydrogen concentration

D_A = apparent diffusivity

$\bar{V}_H$ = partial molar volume of hydrogen in iron

d = grain size

At relatively low stress intensities, intergranular or quasi-cleavage fractures were observed by Beachem (12); Gerberich et al. state that Stage I growth could then be associated with elastic loading where the plastic zone is very small. Here, the long-range hydrogen diffusivity

would be controlled by the elastic stress distribution. The additional assumptions for the Stage I model are:

- a) The plastic zone is within a region less than the grain size.
- b) The crack nucleates at one grain.
- c) The hydrogen collects in this grain from the immediately surrounding grains; $(dp/dx)_{\text{elastic}} < 0$.
- d) The crack grows intergranularly, one grain at a time.
- e) The growth step occurs when $C_0 \rightarrow C_{cr}$.
- f) Short-time diffusion kinetics are applicable.

The time between crack jumps, Δt_s , is given by

$$\Delta t_s = \frac{(C_{cr} - C_0) d RT}{3C_0 D_A \bar{V}_H dp/dx} \text{ and } \frac{da}{dt} = \frac{3C_0 D_A \bar{V}_H (dp/dx)}{(C_{cr} - C_0) RT} \quad (2)$$

and the hydrogen pressure tensor, $(dp/dx) = 2K(1+\nu)/9d^{3/2}$. Substitution yields equation (1) above. The salient features of this equation are:

- 1) Stage I kinetics are linear with K .
- 2) $(da/dt)_I \propto (1/T)$
- 3) $(da/dt)_I \propto (1/d^{3/2})$
- 4) $(da/dt)_I \neq f(\text{yield stress})$

Conversely, Stage II kinetics are independent of stress intensity and vary linearly with yield stress and inversely with grain size:

$$(da/dt)_{II} = \frac{9C_0 D_A \bar{V}_H \sigma_{ys}}{2d RT (C_{cr} - C_0)} \quad (3)$$

Stage II was found to be plastically controlled, with the following assumptions:

- 1) The plastic zone exceeds several grains.
- 2) The crack tip blunts and a plastically constrained region forms.
- 3) Hydrogen flows away from the crack tip to approximately a grain length in front; $(dp/dx)_{\text{plastic}} > 0$.
- 4) Assumptions b) through f) for Stage I hold for Stage II.

For this plastically controlled stage, $(dp/dx)_{II} = 3\sigma_{ys}/2d$, and substitution into equation (2) yields equation (3) above for Stage II kinetics. Once again, the most important feature of this relationship is the independence of the kinetics on stress intensity, and its linear dependence on yield stress.

Stage III kinetics are plastically controlled as in Stage II, but the following assumptions are made:

- 1) The distance the crack jumps in a single step is not controlled by grain size since the fracture mode changes to ductile rupture at high K.
- 2) The crack nucleates intergranularly, but the growth step occurs by ductile rupture.
- 3) Other assumptions remain the same.

Here, the crack jump distance is given by:

$$\ell_{cr} \cong \frac{K^2}{\sigma_{ys} E} \text{ and } (dp/dx) = \frac{3\sigma_{ys}}{2d}$$

Substitution into equation (2) yields the expression for Stage III kinetics:

$$(da/dt)_{III} = \frac{9C_o D_A \bar{V}_H K^2}{2Ed^2 RT (C_{cr} - C_o)}$$

It is seen that Stage III kinetics revert to a highly stress-intensity dependent process, i.e. $da/dt \propto K^2$. Also, the rate varies as d^{-2} and is again independent of yield stress.

Landes and Wei (40) also found the crack kinetics to be strongly dependent on stress intensity, but only above K_{Th} (no cracking below K_{Th}). However, at very high K values, they found (da/dt) to be independent of K , and reaching a limiting value. The rate limiting crack velocity suggests that crack growth is controlled by a rate limiting process, which Landes et al. propose to be a hydrogen permeation process. This three-step process consists of:

- 1) A metal-water reaction or atmosphere which makes hydrogen available.
- 2) Entry of hydrogen into steel.
- 3) Diffusion of hydrogen to a highly stressed crack tip region.

Besides finding a limiting value of crack velocity, Landes formed the following conclusions:

- a) K is relatively insensitive to temperature changes.
- b) Velocity is thermally activated with an apparent activation energy that depends on K .

- c) K_{Th} is independent of temperature.
- d) There is an incubation period at the onset of loading where growth rates are slower than expected.
- e) (dp/dx) is always negative, i.e., hydrogen always diffuses towards the crack tip.

The last conclusion does not agree with Gerberich, et al., who found (dp/dx) to be negative only for Stage I elastic processes, and positive for Stage II and III.

On the basis of measuring crack growth by electric potential (ep) methods, Landes found the crack length to be described by:

$$a_{ep} = a - \int_0^{a-a_0} f[v(r)]dr$$

and

$$\frac{da_{ep}}{dt} = \frac{d}{da} \left(a - \int_0^{a-a_0} f[v(r)]dr \right) \frac{da}{dt}$$

Solving for da/dt yields rates with a reported accuracy of better than +10%.

Lessar and Gerberich (41) investigated grain size effects on crack velocity and found that increasing grain size decreases crack growth kinetics due to a diffusion limiting process (since the amount of failure by tear did not increase as the yield stress decreased); this appears to be similar to the findings of Landes et al. In addition, Lessar investigated the effects of prior γ grain size and concluded that it has a large effect on da/dt plus a mild effect on K_{ISCC} and K_{Th} .

Stepanov et al. (46) took a slightly different approach and created a mathematical model for endurance time instead of crack growth rate.

For static loading, the relationship is:

$$\tau = \tau_0 \exp [(U_0 - \gamma\sigma)/KT]$$

where U_0 = activation energy

σ = average stress

$$\tau_0 = 10^{-13} \text{ c}$$

$\gamma\sigma = Vn\sigma$, where

n = coefficient of the overstress, and

V = activation volume.

Therefore, a small change in stress gives a large change in endurance time. After investigating the effects of cyclic loading also, Stepanov proposed this relationship:

$$\sum_{i=0}^{n-1} \int_0^{t_n} dT/\tau_0 \exp ([U_0 - \gamma(n_i\sigma - \alpha \ln (t/t_0 + 1))]/KT) = 1$$

and $\tau_i = Nt_n$

t_n = time for load impulse.

n_i = coefficient of overstress at the beginning of the i^{th} cycle.

t = loading time.

t_0 = initial loading time.

τ_i = endurance time for cyclic loading.

After comparing static and cyclic loading, Stepanov states that for cyclic loading the failure probability for a given time is much greater

than for static loading. Also, failure during cyclic processes can be expected to occur at stresses where failure would not occur under static loading.

Nakasa et al. (47) also studied the effect of repeating loads on crack growth kinetics. After first stating that (da/dt) for delayed failure under a repeating load is smaller than that under static loading, Nakasa gives the relationship:

$$\left(\frac{da}{dt} \right)_{\text{cyclic}} = 2f \int_0^{1/2f} \frac{da}{dt}(K) dt$$

f = frequency of repeating load.

$\frac{da}{dt}(K)$ = crack propagation rate under static load.

and given this rationale: Repeating load changes the position of the region with triaxial tensile stress cyclicly, and disturbs the concentration of hydrogen atoms to the region. This delays the occurrence of hydrogen cracking. Furthermore, the generation of compressive retained stress or the change of microstructure near the crack tip due to repeating load will suppress the invasion and diffusion of hydrogen atoms.

Crack growth rate is a complex function of " f " (frequency of repeating load) and " ΔK " (range of stress intensity factor). The incubation time is also dependent on ΔK , decreasing as ΔK increases, because a repeating load promotes a continuing corrosion reaction on the notch surface due to the fragmentation of oxide films, and also facilitates adsorption and ingression of hydrogen atoms into the material.

Other conclusions by Nakasa et al. are:

- 1) Incubation time decreases as K increases, and K increases with (da/dt) for static loading.
- 2) Incubation time and K_{ISCC} are decreased by the superposition of repeating load as ΔK or f increase. The controlling mechanism of these behaviors is likely the promotion of a corrosion reaction on the crack tip by the repeating load.
- 3) (da/dt) in delayed failure is decreased by the superposition of repeating load, and there are two valleys of crack propagation rate minima on the (da/dt) - f or (da/dt) - ΔK curves.

Williams (53) described an alternative approach to K_{Th} as a basis for establishing realistic failure criteria for components subject to environment induced crack growth. His method utilizes a fracture mechanics analysis but does not depend on the assumption of a specific value of "threshold" stress intensity. Williams assumed the usual idealized relationship between stress intensity and crack growth for conditions of constant environmental variables in which da/dt is strongly dependent on stress intensity level in Stage I, while in Stage II the crack growth rate is essentially independent of stress intensity. Considering only Stages I and II, and assuming the crack growth rate is determined by the slower of two rate processes operating in series, the following equation was developed for the time to fracture:

$$t = \frac{a-a_0}{C_2} \frac{2}{C_1 \sigma^2 \phi^2} \left(\frac{\sigma \phi a^{\frac{1}{2}} + 1}{e^{\sigma \phi a^{\frac{1}{2}}}} - \frac{\sigma \phi a_0^{\frac{1}{2}} + 1}{e^{\sigma \phi a_0^{\frac{1}{2}}}} \right)$$

$$\text{where } \phi = mM \left(\frac{\pi}{Q} \right)^{\frac{1}{2}}$$

C_1 , m , and C_2 are all undefined parameters which are independent of K_I (and therefore of a) but which may depend on temperature and other environmental variables.

The equation was proposed as a basis for calculating instantaneous crack length, a , at a gross stress level for any specified time of exposure t and initial crack length, a_0 ; or to calculate the more useful parameter $\left(\frac{a_0}{a_c} \right)^{\frac{1}{2}}$ for specified values of t and a_c . The parameter $\left(\frac{a_0}{a_c} \right)^{\frac{1}{2}}$ is equivalent to the ratio $\frac{K_{Ii}}{K_{Ic}}$ at specified values of t and K_{Ic} . Consequently, this approach attempts, by means of an analytical expression, to relate failure time for given environmental conditions to the initial crack length a_0 and the critical crack length a_c or alternatively to the initial stress intensity and the plane strain fracture toughness for a given material. Williams used experimental data for the hydrogen induced cracking of the Ti-5Al-2.5Sn alloy to verify the form of and to establish values of the constants in the analytical expression. He concluded that the predicted effects were in general agreement with the experimental results for this particular alloy and one particular case of environment induced cracking.

RELEVANT FRACTURE TOUGHNESS TESTS

Introduction

The resistance of metals to hydrogen-induced embrittlement and delayed fracture is not reliably predicted on the basis of conventional short-term tensile testing methods. Materials exhibiting a reduction in ductility due to thermal or mechanical processing do not necessarily exhibit an increased susceptibility to slow crack growth, and conversely no change in conventional mechanical properties such as ductility is any assurance that a material will not exhibit slow crack growth. The very nature of hydrogen embrittlement processes, viz. the diffusion of hydrogen to regions of high stress intensification, points to the importance of considering the failure process in terms of the conditions influencing crack initiation and crack growth rates. As indicated in Table I, a large number of investigations conducted over the past decade have indicated that slow crack growth in steels and other materials pre-charged with hydrogen or containing residual concentrations of hydrogen can be studied by employing the methods of fracture mechanics.

The prediction of material integrity for canister applications extending over a period of 500 to 1000 years imposes practical limitations on the test methods that can be employed for material evaluation. The limited sensitivity of crack growth measurement techniques makes it extremely difficult to detect sub-critical crack growth at stress intensities well below K_{IC} . The long test times required for the accumulation of meaningful crack growth data at low stress intensities impose severe restrictions on this method as a basis for assessing the resist-

ance to delayed failure; furthermore, important questions arise regarding the validity of using accelerated crack growth tests as a basis for predicting the long time behavior expected under much less severe loading conditions. Many workers have reported the existence of a threshold stress intensity K_{Th} below which crack growth due to hydrogen increase or redistribution does not occur. The existence of a threshold stress intensity for hydrogen-induced cracking in both hydride forming and non-hydride forming metals indicates that the determination of the conditions required to completely exclude slow crack growth can be used to compare the resistance of various materials to delayed fracture. However, when applying the methods of fracture mechanics including the determination of K_{Th} values, specimen geometry considerations become extremely important, especially in those cases where plane strain conditions do not exist, e.g., mixed mode and plane stress fracture conditions. The majority of the test data is based on specimen configurations that satisfy plane strain fracture conditions, and there is a paucity of information available regarding long term resistance to delayed fracture for specimens of low thickness where plane strain conditions do not exist.

Crack Growth Measurement and the Threshold Stress Intensity K_{Th}

A number of recent investigators (e.g. 22,34,40,41,43,44,47,48) have examined the relationship between crack growth rate and stress intensity as a basis for defining the threshold conditions which yield a value of K_{Th} . A variety of methods have been employed by different investigators to measure crack growth rates, transient effects and the

conditions corresponding to crack initiation and arrest. The time of testing is an important limitation in such methods, and tests consuming in excess of 1000 hours are not uncommon for the purpose of detecting extremely slow crack growth and for determining threshold critical stress intensity values. Table II is a compilation of the test methods for crack length measurement compiled by Deans and Richards (54). Included in the list is a recently developed method employing strain gauge configurations on the back face of compact tension (CT) and T-type wedge opening loading (WOL) specimens. This method permits measuring crack length when the load is known or measuring load when the crack length is known; the technique is extremely sensitive and has been employed in a recent investigation by Akhurst and Baker (48) for examining sub-critical crack growth close to the threshold stress intensity during hydrogen-induced cracking in Ni-Cr-Mo-V steels. Table II also includes a brief description together with the advantages and disadvantages for each of the common methods of crack length measurement (55-70).

The phenomenon of "crack tunnelling" has been a frequent observation in the slow crack growth accompanying hydrogen-induced failure in titanium alloys. Table III summarizes a number of fracture mode observations (21-30, 71-79), some of which were discussed in a previous report (31). Crack tunnelling observations are noted in several investigations and point to the inadequacy of the free surface observations in monitoring the slow growth of cracks in specimens where there is a significant difference in crack advance between the mid-thickness and the outer surface. The observations listed in Table III were discussed in detail previously (31); it is evident from the tabulation that crack

propagation leading to delayed fracture is associated with hydrogen redistribution to points of high stress intensity. Furthermore, beta phase networks in alpha/ beta and near-alpha alloys worsen the situation by providing preferred paths for hydrogen diffusion; the results also reveal that cracking is generally initiated at or near the alpha/beta interfaces. The recent TEM study by Koike and Suzuki (32) on vanadium has clearly shown the dependency of step-wise crack propagation on the formation and cleavage of hydride particles in the vicinity of a crack tip. These investigators further suggest that ordered arrangements of hydrogen atoms on (110) due to long range elastic interactions can account for the slow crack growth process observed in iron and steels due to hydrogen effects. They have compared the role of such ordered arrangements comprising a few hydrogen layers near a crack tip to the formation of hydride precipitates in other metals such as vanadium or titanium.

Table I which was introduced in a previous section of this report summarizes a number of recent observations pertaining to hydrogen-induced crack growth leading to delayed fracture in a variety of alloys. Appendix I provides a more detailed summary and commentary on each of the investigations listed in Table I. Nearly all of the recent investigations have employed threshold stress intensity measurements as a basis for defining the conditions leading to hydrogen embrittlement and delayed fracture. Tables IV and V list some of the strengths and weaknesses of K_{TH} as a criterion for predicting delayed fracture. The following important conclusions can be drawn from the observations cited in Tables I, IV, and V, and Appendix I.

- 1) Under conditions of plane strain, crack growth is expected to occur only when K_{Applied} is greater than K_{Th} .
- 2) The value of K_{Th} depends on environmental conditions, microstructure, yield stress, notch radius, temperature, residual stresses, and textures. Specimen thickness is also an important consideration, especially in those cases that do not comply with plane strain conditions.
- 3) Measurements of ΔK_{Th} have been proposed as a more conservative basis by some investigators (46,80-83) for determining crack growth resistance.
- 4) The kinetics of crack growth in the vicinity of the threshold condition have not been studied extensively; however, recent observations indicate that cracks may experience alternating fast and slow growth near the threshold condition, and the repeated nucleation of microcracks may occur ahead of the main crack front.
- 5) The occurrence of transient crack growth following load increases below K_{Th} has been suggested by Akhurst and Baker (48).

Williams (53) and Wanhill and Van Leeuwen (45) commented on the questionable value of K_{Th} as a parameter that can be considered a material property because it is not as well defined as is K_{IC} due to its dependency on measurement sensitivity, the material, and the environment. Williams proposed an alternative to the "threshold" criterion utilizing fracture mechanics concepts which relate the failure time for given environmental conditions to the initial crack length, a_0 , and

the critical crack length, a_c , for plane strain failure, or alternatively to the initial stress intensity K_{Ii} and the plane strain fracture toughness K_{IC} for a given material. His equation which is described in an earlier section of this report was proposed as an analytical basis for estimating fracture for conditions of time, pressure, and temperature beyond the range of readily available experimental data. Williams acknowledged that the application of his equation would require further experimental verification and that "the degree of realism of the prediction would vary from system to system." Although Williams demonstrated the usefulness of the equation for describing the conditions for hydrogen-induced cracking of the Ti-5Al-2.5Sn alloy, his approach does not seem to have been developed or applied by others in the recent available literature.

Investigations of the influence of microstructure on the value of K_{Th} have been limited to a few specific studies involving grain size effects and microstructural changes intended primarily to modify the yield strength. Lessar and Gerberich (41) investigated the effects of prior austenite grain size on the hydrogen embrittlement of 4340 steel and reported that increased grain size led to an increase in the value of K_{Th} . They also developed a quantitative relationship in which the crack velocity is proportional to $\frac{1}{d^2}$ (where d is the grain diameter). Microstructural effects were also considered by Doig and Jones (42) who reported that the threshold value K_{Th} decreased as a result of heat treatment intended to increase the yield strength and increased with increasing notch radius. These latter investigators defined a critical

distance (d_c) corresponding to a "microstructural feature associated with cracking."

Wanhill and Van Leeuwen (45) reported that the value of K_{Th} in titanium alloys may be affected by "dwell cracking" and by crack micro-branching" thereby suggesting that the value of K_{Th} is sensitive to the test procedures. The work of Nakasa et al. (47) on Ni-Cr-Mo steels points to the potential importance of test procedures involving repeated loads in determining the threshold conditions for delayed failure in steels. Their investigation revealed that crack propagation can be reduced by repeating loads and attributed this result to the changing position of the triaxial stress state and the generation of compressive retained stress in the region of the crack tip. The results of Nakasa et al. cast some doubt on the general usefulness of ΔK test methods for determining the threshold condition without supporting information from sustained load measurements of K_{Th} .

Although most investigators acknowledge the importance of residual stresses and texture effects, the available literature does not record systematic investigations of these parameters. Simpson and Puls (33) have pointed out that the crack velocity can be altered by residual stresses or by crack blunting in zirconium-niobium alloys. Boyer and Spurr (30), in an investigation of Ti-6Al-4V alloys reported a strong orientation effect on the threshold conditions for hydrogen induced cracking. In both titanium-base and zirconium-base alloys, it is apparent from the work of Boyer and Spurr and that of Simpson and Puls that crack growth is controlled primarily by hydride precipitation; however,

hydride orientation and morphology may be important parameters affecting the crack growth rate.

The limitations of existing detection methods such as those in Table II make it difficult to prove whether the complete arrest of cracks has in fact occurred and whether such arrest will persist over the prolonged periods involved in nuclear waste containment. The recent observations of Akhurst and Baker (48) indicate the need for a closer examination of the physical significance of experimentally determined K_{Th} values. They obtained fractographic evidence of alternating fast or slow crack growth near K_{Th} and interpret this as an indication that cracks advance by the repeated nucleation of microcracks at microstructural features ahead of the main crack. They also reported transient crack growth following increases in load just below the value of K_{Th} and concluded that there is no simple transition from zero crack growth to sustained growth. In this respect the use of K_{Th} values as a basis for material selection for long term resistance to delayed fracture will have to be considered with great caution. The reason for this conclusion is amplified even further by the observation of transient growth effects followed by arrest under conditions close to the K_{Th} value. The uncertain sensitivity of these transient effects to temperature, microstructure, and environmental conditions may prove to be very treacherous in employing K_{Th} values as a basis for design.

Plane Strain versus Elastic/Plastic Failure Conditions

Most investigators have been concerned with plane strain conditions in defining criteria for the onset of slow crack growth. The resulting

values of the threshold stress intensity are not expected to apply to those cases where elastic/plastic conditions exist. When comparing the threshold conditions for cracking in various materials, it is important to realize that quasi-elastic conditions are less likely to be satisfied as the yield stress is decreased; another important consideration is material thickness since components of small thickness may exhibit either mixed mode or even plane stress conditions in which plastic deformation assumes an important role in the fracture process. While elastic stress analyses have been highly developed and applied in the determination of K_{IC} and K_{Th} values, there has been more limited success in developing elastic/plastic analyses where fracture initiation and instability do not usually coincide. In the latter case, as the thickness of a plate is decreased, the notch toughness increases even though the metallurgical characteristics of the material are unchanged.

For many structural materials and alloys, the flaw sizes required for catastrophic fracture are greater than those that might escape initial detection; however, under alternating loads initial cracks of subcritical dimensions may undergo progressive growth and such conditions are particularly important in large welded structures or other fabricated forms in which residual stresses of considerable magnitude exist. By employing the methods of fracture mechanics, it is possible to ensure that the number of cycles of loading required to grow a small crack to a critical crack dimension is greater than the design life of the structure. The procedure described by Rolfe (81) for the analysis of crack growth behavior in steels and weld metals using fracture mechanics concepts is as follows:

1. On the basis of the quality of inspection, estimate the maximum initial flaw size a_0 present in the structure and the associated K_I relation for the member being analyzed.
2. Knowing K_C or K_{IC} and the nominal maximum design stress, calculate the critical flaw size a_{cr} that would cause failure by brittle fracture.
3. Obtain an expression relating the fatigue crack growth rate of steel or weld material being analyzed; for example, conservative estimates of fatigue growth per cycle of loading $\frac{da}{dN}$ have been determined for martensitic steels as well as ferrite-pearlite steels in a room temperature air environment.
4. Determine K_I using the appropriate expression for K_I , the estimated initial flaw size a_0 , and the range of live load stress (cycle fatigue stress).
5. Integrate the crack growth rate expression between the limits of a_0 (at the initiation of K_I) and a_{cr} (at K_{IC}) to obtain the life of the structure before failure.

The fracture mechanics approach also provides a quantitative method for analyzing material behavior under conditions of alternating stress in the presence of hostile environments. The progressive growth of small cracks during the life of a structure may be intensified by the presence of stress corrosion cracking conditions or hydrogen embrittlement; such conditions can aggravate the effect of subcritical crack growth induced by fatigue loading conditions. The corresponding critical values of the stress intensity are identified as either K_{ISCC} or K_{Th} , as discussed in other sections of this report. The K_{ISCC} value is

frequently used as a failure criterion rather than K_{IC} when the former value is applicable to crack growth in a particular environment. However, Rolfe (81) has pointed out that values of K_{ISCC} , while they may be useful for certain specific applications "have not been used in general design applications because the long-range significance of K_{ISCC} values with respect to the service performance of structures has not been established."

K_{IC} values determined by linear elastic analyses are not applicable under conditions of general yielding where large plastic zones are formed in the region adjacent to a moving crack. Such conditions may exist in many low and medium strength structural steels where the section sizes are insufficient to maintain plane strain conditions under slow loading rates and at service temperatures above the ductile-brittle transition range. It is then necessary to employ extensions of the methods of linear elastic fracture mechanics (LEFM) such as the following:

1. R-Curve analysis (31,81,82,84,85). This method permits the determination of K_C , the critical stress intensity factor for fracture under plane stress conditions.
2. Crack opening displacement (COD) (82,84). This method involves a measure of the prefracture deformation that occurs at the tip of a sharp crack.
3. J integral (82,84,86). This analysis involves a determination of the path dependent integral which is an average measure of a combined elastic/plastic stress strain field ahead of a crack.

Each of the above methods has been reviewed extensively in the literature and were summarized in the earlier report (31); however, most researchers readily acknowledge that while the methods of elastic/plastic analysis offer considerable future promise in design, the current state of knowledge is relatively undeveloped in comparison to the concepts of linear elastic fracture mechanics. One of the major limitations relates to the difficulty of translating laboratory data to actual design situations.

This point is illustrated clearly by the case of slow crack extension in which the crack advances at first slowly when the local stress reaches a certain critical value, and as the local stress increases the rate of crack extension increases. In a thick plate the crack front penetrates more in the mid-thickness than at the surface in a manner typical of "tunnelling." This mechanism results in a more intense state of stress in the decohesion enclave which can eventually lead to catastrophic fracture by "decohesion." Consequently, an increase in the observed size of a crack by crack movement is not the only important consideration, since increased severity of the stress system in the enclave at the midpoint of the specimen thickness can be the dominant factor in determining the susceptibility of a material to eventual catastrophic fracture. The importance of considering this point in dealing with the problem of slow crack growth was emphasized a number of years ago by Boyd (87).

The application of the methods of fracture mechanics to analyze the fatigue life and crack growth resistance of structural components has also been limited by an inability to include in a quantitative way the

influence of combined cyclic loading and complex crack geometries, especially where the direction of crack growth is not obvious. This problem has been considered by Sih (88) who has proposed a method for predicting subcritical crack growth under conditions of fatigue loading where a crack can change its direction of propagation. This effect is an important consideration in a number of design applications involving aircraft, ships, containment vessels, etc., where the loading direction can vary with respect to crack orientation during service.

Recommended Predictive Test For Plane Strain Conditions

An adequate test for monitoring and predicting delayed failure due to hydrogen and stress corrosion cracking must provide the opportunity to examine the influence of a number of related yet clearly defined parameters, including the following:

1. Exposure temperature
2. Chemical environment
3. Hydrogen content
4. Crystallographic texture
5. Applied load
6. Prolonged exposure times

The work of Boyer and Spurr (30) demonstrated the versatility and usefulness of the double cantilever beam (DCB) technique for examining crack growth processes that occur over long periods of time. This testing technique can be used to examine the six parameters listed above; Boyer and Spurr monitored crack growth over periods in excess of one year in DCB specimens of the Ti-6Al-4V alloy.

The specimens were fatigue precracked, following which they were pin loaded in an Instron test machine to the desired K levels. The load was then maintained by means of adjustable bolts, thereby creating a specimen in which the stress intensity decreases with crack extension. The stress intensity was calculated using the following standard formula derived from beam theory:

$$K = \frac{\Delta E h [3h(a+0.6h)^2 + h^3]^{1/2}}{4[(a+0.6h)^3 + h^2 a]}$$

where K = stress intensity

Δ = specimen deflection across loading center line

E = Young's modulus

h = specimen height

a = crack length measured from bolt center line

The change in crack length of pre-loaded specimens was monitored by means of an optical microscope. Although this method is restricted to the observation of surface growth rates, it was argued that faster absolute crack growth rates due to tunnelling effects will also be manifested in the form of faster surface rates. Alternatively, there are a number of other techniques available for monitoring crack growth as summarized in Table II. It is therefore possible to test a number of specimens simultaneously as a basis for examining crack growth under a variety of loading conditions or environmental parameters. For example, specimens can be pre-charged with varying levels of hydrogen concentration prior to loading and testing. Alternatively, specimens in a given condition of heat treatment can be loaded to a variety of predetermined

K levels and then subjected to selected environmental conditions for varying periods of time.

The specimen configuration employed in this test is convenient for examining the effects of temperature variation and changing environmental conditions on the rate of crack growth during the period a material is subjected to sustained load conditions. The technique offers several important advantages including relatively low specimen cost and the fact that mechanical testing facilities are only needed to pre-load the specimens. In this way it is possible to test a large number of specimens concurrently.

CONCLUSIONS AND RECOMMENDATIONS

1. Significant progress has been realized in the development of diffusion models to predict crack growth rates in hydride forming metals, but each model appears to suffer from some form of uncertainty because of the assumptions and approximations that must be made. The 1977 version of the Simpson-Puls-Dutton model appears to be the most amenable with respect to utilizing known or readily estimated quantities, but like the other models it does not provide a means for predicting crack initiation or threshold conditions. The Pardee-Paton model requires extensive calculations involving estimated quantities; qualitative agreement has been shown with some experimental data.
2. Recent observations by Koike and Suzuki on vanadium support the general assumption that crack growth in hydride forming metals is determined by the rate of hydride formation. Their hydrogen atmosphere-displacive transformation model is of potential interest in explaining hydrogen embrittlement in ferrous alloys as well as hydride formers. This model merits continued investigation, especially with respect to experiments on bulk specimens.
3. The discontinuous nature of cracking due to hydrogen embrittlement appears to depend very strongly on localized stress intensities (i.e. on a microstructural scale), thereby pointing to the importance of considering the role of microstructure in influencing crack initiation, fracture mode and the crack path. Important microstructural parameters include the grain size, the size, shape, and dis-

tribution of brittle second phase particles (including precipitates), and textures.

4. The initiation of hydrogen induced failures over relatively short periods of time can be characterized with fair reliability by employing measurements of the threshold stress intensity K_{Th} or ΔK_{Th} , the latter being determined under conditions of alternating load. The usefulness of these parameters for predicting material integrity over periods ranging from 500 to 1000 years is somewhat less reliable, especially under conditions where the redistribution of internal hydrogen or hydrogen pick-up can occur.

The experimental conditions for determining K_{Th} and ΔK_{Th} are designed to ensure plane strain conditions in most cases and do not necessarily model the problem at hand with respect to canister applications. In particular, the stress levels expected under canister containment conditions are extremely low, and environmental conditions are subject to change over prolonged periods of time. However, plane strain test conditions may be viewed as a conservative basis for predicting delayed failure.

5. The physical configuration of nuclear waste canisters may involve elastic/plastic conditions rather than a state of plane strain, especially in those applications involving thin-walled vessels. Under conditions of elastic/plastic failure, alternative predictive tests may be considered, including COD and R-curve methods.
6. The long test times necessary to accumulate meaningful crack growth data at low stress intensities currently limit the development of reliable tests for predicting delayed failure under nuclear waste

containment conditions. The double cantilever beam technique employed by Boyer and Spurr on titanium alloys offers definite advantages for examining hydrogen induced delayed failure over long periods of time. This test method permits a large number of specimens to be evaluated concurrently and at relatively low cost.

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Table I. Summary of Experimental Observations
Crack Growth and Crack Growth Rates

<u>Investigators</u>	<u>Material</u>	<u>Observations</u>
Landes and Wei (40) 1973	4340 steel tempered at 400°F	<ul style="list-style-type: none"> - Crack growth occurs only for $K > K_{Th}$. - Crack growth in distilled water shows strong K dependence at lower values of K and reaches constant rate limiting value at higher K levels. - Rate limiting step not defined.
Lessar and Gerberich (41) 1976	4340 steel	<ul style="list-style-type: none"> - Prior austenite grain size effects studied. - Increased grain size (i.e. greater than plastic zone), increased K_{Th}. - Crack velocity proportional to $\frac{1}{d^2}$ (d is grain diameter). - Crack growth kinetics affected mostly by diffusion limiting process related to either "size of grain boundary region" or degree of retained austenite.
Doig and Jones (42) 1977	Steels (Austenitic)	<ul style="list-style-type: none"> - K_{Th} decreased with increasing yield strength. - K_{Th} increases with increasing notch radius. - "Critical distance" d_c defined by "microstructural feature associated with cracking." - K_{Th} has lower limit with decreasing notch radius ρ that is determined by length parameter d_c. - For $K_{APPLIED} = K_{Th}$ an infinite time required for embrittlement.
Gerberich, Chen, and St. John (43) 1975	4340 steel	<ul style="list-style-type: none"> - Stage I--stress intensity dependent--growth kinetics controlled by elastic stress field. - Stage II--nearly independent of stress intensity--growth kinetics controlled by plastic stress field. - During Stage II decrease in crack growth rate attributed to increase in crack tip radius as stress intensity is increased. - Prediction that H diffusion decreases with increasing K during Stage II.
Gerberich and Chen (44) 1975	4340 steel Maraging and 9Ni-4Co steels	<ul style="list-style-type: none"> - Applied stress intensity equals K_{Th} when equilibrium concentration of H at the crack tip achieves the critical concentration required for embrittlement.

<u>Investigators</u>	<u>Material</u>	<u>Observations</u>
		$K_{app} < K_{Th} \rightarrow C_{eq} < C_{cr}$ and no cracking. $K_{app} > K_{Th} \rightarrow C_{eq} > C_{cr}$ equilibrium not achieved and cracking proceeds.
Wanhill and Van Leeuwen (45) 1978	Ti Alloys	<ul style="list-style-type: none"> - K_{Th} in Ti affected by "dwell cracking"--sustained load cracking during hold or dwell at maximum load in fatigue cycle is followed by propagation during dwell at lower stress intensities. - K_{Th} affected by crack "microbranching" and K_{Th} value sensitive to test procedure.
Stepanov et al. (46) 1979		<ul style="list-style-type: none"> - For cyclic loading--failure probability for a given time is much greater than for static loading. - Lower stresses for failure under cyclic loading.
Nakasa, Takei, and Kido (47) 1977	Steel-NiCrMo quenched and tempered	<ul style="list-style-type: none"> - Incubation time decreased by repeating loads as ΔK or f increased. - Crack propagation rate decreases by repeating load. - Two valleys of crack propagation rate: <ol style="list-style-type: none"> 1) Changing position of triaxial stress state. 2) Generation of compressive retained stress near crack tip.
Boyer and Spurr (30) 1978	Ti-6Al-4V	<ul style="list-style-type: none"> - Crack growth rates < 0.1 mm/day stabilized. - Crack growth rate temperature sensitive. - For fixed T crack growth rate increases with H content. - Strong orientation effect suggesting textures are important. - Stress intensity above K_{Th} does not assume an important role suggesting that once started, crack growth is controlled by hydride precipitates.
Simpson and Puls (33) 1979	Zr-2.5%Nb	<ul style="list-style-type: none"> - Crack velocity sensitive to crack tip stress pattern. - Crack velocity can be altered by residual stress or by crack blunting. - Crack velocity dependent on test temperature with respect to solubility temperature. - Hydride morphology may be an important parameter affecting crack growth rate. - Stage I velocity vs. K very steep. - Stage II relatively insensitive to K.

<u>Investigators</u>	<u>Material</u>	<u>Observations</u>
Moody and Gerberich (22) 1980	Ti-6Al-6V-2Sn	<ul style="list-style-type: none"> - Crack growth rate $\frac{da}{dt}$ shows three-stage dependence on K. - For K near K_{Th}, $\frac{da}{dt}$ shows strong dependence on K and T. (Exponential dependence on K with maximum rate at 300°K.
Akhurst and Baker (48) 1981	Steels 3.5% NiCrMoV quenched and tempered	<ul style="list-style-type: none"> - Alternating fast and slow crack growth near K_{Th}. - Repeated nucleation of microcracks ahead of main crack. - Transient crack growth following load increases below K_{Th}. - Zero crack growth rate for $K < K_{Th}$ supported by cutoff in crack rate vs. K and clear distinction with Stage I. - Conclude equilibrium arguments valid at K_{Th}.

Table II. Summary of Methods of Crack Length Measurement (54).

Technique	Brief Description	Advantages	Disadvantages
Optical	relies on microscopes or telescopes, often aided by etched or scribed markings; almost all test piece geometries	Inexpensive; does not require calibration; does not require specimen to behave in a linear elastic manner	only gives surface readings and usually underestimates average crack length because of crack curvature; not amenable to automation and hence time-consuming; requires surfaces to be accessible and in well-polished condition
Mechanical, COD	basis is to measure the COD, usually between points along the loading line or, in the case of bend and wedge opening loading specimens, at the front face [55-60]; displacement measured mostly by clip gages; for high temperature testing extension arms may be used to transfer the displacements to lower temperature regions for measurement; extension arms may be used via moving seals to measure displacements inside autoclaves; any test piece geometry that behaves in a linear elastic manner	cost depends on application and ranges from low cost in room temperature air to moderately expensive in high temperature aggressive environments; does not require the specimen to be visually accessible and can provide an average crack length figure; easily incorporated in automatic systems	calibration required in some cases: clip gages and to a lesser extent transducers not very robust
Mechanical, BFS	strains measured on the back face of CT or T-type WOL specimens by strain gages or possibly clip gages or transducers for large test pieces; possible use in single-edge-notched tension or three and four point bend specimens; all specimens must behave in a linear elastic manner	cost depends on application and ranges from very inexpensive in room temperature air tests to moderately expensive in high temperature aggressive environments; does not require the specimen to be visually accessible and can provide an average crack length figure; shows excellent characteristics for incorporation in automatic systems	calibration required for test pieces other than CT and T-Type WOL specimens
Electrical, strain gage filaments	electrically conducting wires are attached to the specimen so that they are broken by an advancing crack, providing stepwise changes in resistance [61-63]; can be used for all specimen geometries	low cost; easily adapted for automatic processes	only gives surface readings, not well suited for high temperatures and aggressive environments; difficult to locate gages and ensure crack always and only breaks filaments when crack tip passes through

Table II (continued)

Technique	Brief Description	Advantages	Disadvantages
Electrical, d-c potential drop (resistance)	a constant d-c current is passed through a specimen so that a change in crack length alters the potential difference of suitably placed contact points, usually in vicinity of the crack tip [55,64-67]; suitable for all test piece geometries	low cost; does not require any delicate instrumentation attached to the specimen; high stability for long term tests and some relaxation from linear elastic behavior easily accommodated; particularly well suited for automatic control and long term, high temperature testing; robust and simple; can give an average crack length value	some theoretical calibrations available but usual to carry out calibration tests; some uncertainty in stress corrosion and corrosion fatigue studies over possible interference with electrochemical conditions adjacent to crack tip; for decreasing K, constant COD tests crack faces may short electrically, thus underestimating crack length; bridging of crack surfaces by corrosion products may produce erroneous crack length readings; in some cases the grips may have to be electrically insulated from the testing machine; not well suited for very large specimens
Electrical, a-c potential drop (resistance)	similar to d-c potential drop	does not require any delicate instrumentation attached to the specimen; some relaxation from linear elastic behavior easily accommodated; well suited for automatic control and can give average crack length values; high sensitivity	moderate cost; wires have to be carefully placed and must not be moved during test; long-term stability difficult to achieve; bridging of crack surfaces by corrosion products may produce erroneous crack length readings; electrical insulation required
Electrical, eddy currents	an eddy current probe adjacent to a cracked surface produces an electrical signal, indicating the crack [68]; can be used with a servo-system or stepping motor that moves the probe so that a nil eddy current signal is maintained; used for center-cracked sheets but should be adaptable to other geometries.	easily adapted for automatic processes	may only be useful for surface measurements; expensive

Table II (continued)

Technique	Brief Description	Advantages	Disadvantages
Ultrasonic	Involves transmission and reception of a high frequency sound beam intersected by a crack [69]; if probe is fixed the moving crack alters the proportion of the signal reflected by crack and the opposite boundary of the specimen; a more accurate version involves a stepping motor that moves the probe so that the strength of the signal reflected by the crack remains constant [70]; used mainly on WOL compact specimens	can be adapted for automatic processes; internal measurements of crack length; only method that can give crack profile; relaxation from linear elastic behavior easily accommodated	not well suited for small, thin specimens; expensive; cannot be used at high temperatures; not well suited to environmental testing; not a proven technique for specimens other than WOL compact specimens; difficult to achieve high resolution
Acoustic emission	Involves attachment of sensing transducer to test piece that oscillates at its resonant frequency on receiving elastic stress waves from source of deformation [65]; detected emissions are then amplified, selectively filtered and conditioned, and then counted either on a periodic basis as a rate of emission or as a cumulative total; adaptable to any geometry	can be very sensitive for detecting onset of cracking	expensive, sophisticated equipment; filtering of extraneous noise from test machine and grips necessary during testing; poor correlation with crack length; signals are material-dependent

Table III. Hydrogen Embrittlement of Titanium Alloys
Fracture Mode Observations

<u>Investigators</u>	<u>Material</u>	<u>Observations</u>
Refs. (21-30)	α , $\alpha + \beta$	- Evidence for H redistribution to regions of stress intensification and hydride precipitation.
Sandoz (71) 1969	near α (Ti-8-1-1)	- $K_{Th} < K_{IC}$ for H contents from 15 to 50 ppm. - K_{Th} increased by vacuum anneal.
Nelson et al. (72) 1972	α , $\alpha + \beta$	- Crack growth rates depend on external H pressure for continuous β matrix, but not for continuous α . - β paths identified for H diffusion in near α alloys.
Meyn (21) 1974	α , α/β alloys	- K_{Th} decreases as H increases. - Cracking begins at α/β interface. - Cleavage in α phase.
Paton and Williams (23) 1974	Ti-6Al-4V Ti-4Al 100 ppm H	- TEM observation of role of hydride particles. - Hydrogen enrichment at crack tip.
D.N. Williams (73, 74) 1974, 1976	α/β alloys	- Observed crack "tunnelling." - K_{Th} dependent on H content and environment.
Margolin (75) 1976	$\alpha + \beta$	- Applied stress plus H redistribution produces "critical strain" leading to crack nucleation.
Koch et al. (76, 77) 1977-78	near α (Ti-8-1-1)	- Strain rate sensitivity reported. - Similarity of fracture surfaces for stress corrosion and SSRHE.
Boyer and Spurr (30) 1978	Ti-6Al-4V	- Crack propagation associated with hydride/matrix interfaces. - Separation at α/β interfaces. - Crack tunnelling reported.
Peterson et al. (78) 1978	α/β	- Auger analysis showed H induced crack growth in α phase, not at interphase interfaces.
Nazimov et al. (27) 1979	Ti and various alloys	- Stresses $< 0.6 \times U.T.S.$ do not lead to fracture under sustained loads for times $< 17,000$ hours. - Ti-Al offers improved resistance over Ti to H embrittlement.

Table III (continued)

<u>Investigators</u>	<u>Material</u>	<u>Observations</u>
Kennedy, Adler and Schulte (26) 1980	Ti-6Al-4V	- Nuclear microprobe measurement of H concentration along fracture surface. (4-8 x bulk value for slow crack growth).
Moody and Gerberich (22) 1980	Ti-6Al-4V	- Fracture of hydrides with cleaved regions separated by ductile ligaments. - K_{TH} depends on H content and solubility under applied stress.
Hoeg et al. (79) 1980	Ti-6Al-4V	- Large quantities of H (<500 ppm) do not degrade conventional tensile and toughness properties. - Fatigue resistance, stress corrosion and sustained load cracking are impaired. - Two types of strain induced precipitates observed in the plastic zone at the crack tip. - Stress induced hydrides appear to be metastable. Stable γ hydride formation expected after longer times (e.g. 1-2 years).
Koike and Suzuki (32) 1981	Vanadium	- Non-Maxwellian distribution of hydrogen around crack tip with hydride formation due to a displacive transformation. - Cracks propagate in step-wise fashion by repetition of formation and cleavage of hydride particles at crack tip. - Suggestion: In iron and steels ordered arrangement of H atoms on {110} due to long range elastic interactions. - Formation of few H layers near a crack tip resembles hydride precipitate situation. - Crack growth mechanisms in iron may be similar to hydride formers.

Table IV. Criticisms of K_{Th} as a Fracture Criterion

1. K_{Th} is sensitive to a number of parameters, including hydrogen content, temperature stress-state, environment, and microstructural variations.
2. The dependence of K_{Th} on cutoff time is crucial in the prediction of delayed fracture.
3. It is difficult to detect the initial stages of cracking where extremely low growth rates are involved (e.g. incubation period and period of sub-critical crack growth).
4. The confidence in K_{Th} values is limited by observations of alternating slow and fast crack growth near K_{Th} , suggesting that the repeated nucleation of microcracks occurs at microstructural features ahead of the main crack front. (Akhurst and Baker).
5. As the stress intensity is increased toward K_{Th} there is no simple transition from stationary to sustained crack growth. Cracking may initiate, decelerate, and arrest under constant load.
6. Limitations of crack measurement techniques and the possibility of crack "tunnelling" make it difficult to detect transient cracking over long periods of time. Therefore, the complete arrest of cracks is subject to uncertainties requiring conservative design practice.

Table V. Merits of K_{Th} as a Fracture Criterion
due to Hydrogen Embrittlement

1. The crack velocity approaches zero as K is lowered to a limiting value defined as K_{Th} .
2. Crack growth rate increases as the stress intensity is raised above K_{Th} .
3. K_{Th} and the time to failure are increased as the yield strength is decreased.
4. Experiments have confirmed the redistribution of hydrogen by diffusion to regions of high stress intensity.
5. Higher stress intensities are required for crack growth at temperatures where hydride nucleation is reduced because of increased hydrogen solubility.
6. K_{Th} is increased when the hydrogen content in titanium is reduced by vacuum annealing.
7. The relation between stress intensity and crack growth rates depends on whether hydrogen is supplied internally or externally to the region of stress intensification.

APPENDIX

LITERATURE SUMMARIES

CRACK GROWTH AND CRACK GROWTH RATES

LITERATURE SUMMARIES

CRACK GROWTH AND CRACK GROWTH RATES

1. Landes and Wei (40) - 1973

Summary:

- Used AISI 4340 steel tempered at 400°F. Temperature range restricted to 10-75°C.
- Cracks followed by electrical potential, compliance, and optical methods.
- Specimen in distilled water.
- Also used H-11 tool steel, tempered at 950°C--tested only at room temperature.
- Used center-cracked and crack-line-loaded test specimen. "K" is constant for the latter test specimen.
- Calibration for center-cracked specimen is by the secant correction (STP 410).
- Calibration for crack-line-loaded by experimental compliance calibration method.
- Constancy of "K" for crack-line-loaded specimen is $\pm 3\%$.

Conclusions:

- Crack growth in distilled H₂O is controlled by a thermally activated process with apparent activation energies that depend on "K."
- Activation energy is 8000 ± 1000 cal/mole; this is similar to values reported for similar steels.

- This apparent activation energy corresponds to that for hydrogen permeation in AISI 4340, and lends support to the concept that the rate limiting process for crack growth in high strength steels exposed to water is that of hydrogen permeation into the crack tip region.
- Activation energies for crack growth in water and in gaseous hydrogen are different.
- A transient or incubation time exists for specimens initially loaded to high K values.
- During loading, above K_{Th} , the growth rate quickly slows down to a steady-state rate.
- During loading, below K_{Th} , the specimen showed a small amount of crack extension which subsequently stopped completely.
- The above transient growths are only associated with loading, and this is not to be confused with the period of transient incubation growth discussed earlier.
- During loading, there was a short period of transient crack growth which showed much higher growth rates than the sustained load rates.
- Growth rates in gaseous hydrogen are ten times higher than those in distilled water.
- Rate controlling process for crack growth in water is different than that for growth in gaseous hydrogen.
- A variation of 1°C in testing temperature causes a velocity change of 4%. A 5°C change causes a 30% velocity change.

Further Work:

- Effect of tempering temperature should be investigated.
- Use a larger temperature range for testing (instead of just 10-75°C).
- The rate limiting step in the permeation process still needs to be defined. This is since the activation energies in water and in gaseous hydrogen are different.

Critique:

- The crack growth velocity is very dependent on testing temperature. A 1°C and 5°C change causes 4% and 30% velocity changes, respectively. Existence of a rate limiting process also reported by Smith, et al (Eng. Frac. Mech, 1, 1969, pp. 123-128) and by Mostovoy, et al ("A note on SCC Rates," Materials Research Lab., Inc.)
- Calibration compared to analytical calibration of Gross, et al ("Stress Intensity Factors for Crack-line Edge-crack Specimen," NASA Technical Note D-3820, 1967).
- Landes and Wei show results close to those obtained by Gross' boundary collocation technique.
- Accuracy of electrical potential method for crack growth is +50% for crack velocities $\sim 10^{-5}$ in/min., and +10% for velocities $\sim 10^{-3}$ in/min.
- Accuracy of compliance method for crack length determination is +0.005 in.

- At onset of loading, growth rates did not immediately reach expected values. There appeared to be a transient period where growth rates were slower and gradually increased to expected values.
- Specimens initially loaded to high K values showed the transient or incubation time in both test specimen types.
- Reproducibility of growth rates in styrofoam chambers is $\pm 35\%$.
- Crack growth rates less than 10^{-6} in/min hard to measure with any reliability.

2. Lessar and Gerberich (41) - 1976

Summary:

- Estimated K_{Th} by assuming that as $(da/dt) \rightarrow 0$, then $K \rightarrow K_{Th}$.
- Experimentally determined compliance curve to facilitate calculations of "K."

Conclusions:

- Crack kinetics are diffusion limited (which may be related to the size of the grain boundary region, or the degree of retained austenite) and are not due to an enhanced cohesive energy at the grain boundaries.
- Prior austenite grain size has a strong effect on (da/dt) .
- Prior austenite grain size has a mild effect on K_{Th} and K_{ISCC} .
- The effect of increased grain size on decreased crack growth kinetics is diffusion limited.
- Smaller grain sizes displayed a greater amount of failure by tear.

- Impurity (sulfur, phosphorus) effects do not control hydrogen embrittlement processes.
- Increased grain size improves HE resistance if the grain diameter is significantly larger than the plastic zone.
- Tests indicated discontinuous cracking.
- K_{TH} appears to first decrease and then increase with increasing grain size.
- Below $40\mu\text{m}$, K_{TH} is independent of grain size.
- K_{TH} changes with grain size because of the effects of grain size on yield strength and fracture.
- Grain size itself is not the only microstructural parameter controlling cathodically charged HE.
- Failure mode is independent of crack length for a range of "K."

Further work:

- Need a clear description of the "diffusion limiting process" that controls crack kinetics.
- What factors may affect this rate limiting process?
- Can we manipulate these factors to adequately reduce crack growth kinetics to a point where lifetimes of $\sim 10,000$ years are obtained?

Critique:

- The $20\mu\text{m}$ grain-sized material does not follow expected behavior. This was attributed to one of these three possibilities:

- 1) There may have been a difference in the parameters controlling nucleation and growth.
 - 2) There may have been a difference in the amount of impurities segregated at the grain boundaries.
 - 3) Different degrees of retained austenite may have been obtained.
- Heat treatments that produce the desired grain sizes may have also affected other diffusion-limiting processes other than grain structure.
 - Method of estimating K_{TH} may lead to significant error.

3. Doig and Jones (42) - 1977

Conclusions:

- An incubation time precedes cracking.
- Cracking is discontinuous.
- $H_2 \rightleftharpoons 2H$ at root of notch upon loading.
- Diffusion coefficient (D) is independent of stress and concentration.
- For crack initiation, a critical hydrogen concentration (C_C) must be achieved over an unspecified distance, (d_C), determined by the microstructure.
- Apparent threshold stress intensity (K_{ATH}) is the intensity that allows C_C to be achieved over a distance d_C .
- K_{ATH} decreases with increasing yield strength.
- $K_{ATH} \propto \rho^{\frac{1}{2}}$ where ρ = radius of notch root. For mild notches ($d_C \ll \rho$).

- K_{ATH} approaches a minimum for sharp notches (opening displacement and d_c limitations predominate).
- As X_c (peak stress position) increases for increasing K_A , so the time to initiate cracking (t_i) decreases.
- t_i vs. K curve (Fig. 1 in D·J) is displaced to longer times with increasing values of K_{ATH} , ρ and decreasing values of V_H .
- Rate controlling step in HE is the bulk diffusion of hydrogen within the metal lattice.

Other possible rate controlling mechanisms are: the dissociation of hydrogen molecules into atoms at the notch surface, the inhibiting effect of surface oxide films on the transport of hydrogen atoms to the metal surface; the nucleation of the HE crack. These last three mechanisms are shown to be non-rate controlling.

- The critical hydrostatic stress is reached much sooner under conditions of plane strain rather than plane stress.
- HE will occur more readily in thicker sections (where we have plane strain conditions).
- HE behavior is strongly dependent on stress distribution and on microstructure.

Further Work:

- A study of the location of maximum stress (X_c) is needed.
Does it exist at the elastic-plastic boundary or within the plastic zone?
- Study effects of stress and concentration on the diffusion coefficient (D).

- Clarify the meaning of d_c , the critical (unspecified) distance. Also, how is d_c affected by microstructure and other variables?

Critique:

- Does X_c exist at the elastic-plastic boundary? Gerberich, Chen, and St. John (43) state that recent analyses have shown that the highest stress (X_c) and highest concentration exist within the plastic zone.
- Is diffusion coefficient (D) really independent of stress and concentration?
- d_c term is ambiguous and needs clarification. Is it independent of everything except concentration and stress intensity?

4. Gerberich, Chen, St. John (43) - 1975

Summary:

- Study employed 4340 steel tempered in a 200-500°C range.
- Used grain diameter as a size parameter in estimating crack growth kinetics (since the actual grain size laid in the range of X_{cr}).

Conclusions:

- The hydrostatic stress field at the tip of a crack is a major component if not the controlling parameter in HE processes.
- Stage I is bypassed at high tempering temperatures.
- Stage III is bypassed at low tempering temperatures (since their low fracture toughness caused instability in Stage II).

- Stage I is ~100% intergranular failure.
- Stage II exhibits more ductile rupture as K increases.
- Stage III is predominantly ductile rupture failure.
- The pressure tensor gradient (dp/dx) acts as a driving force for hydrogen diffusion, so diffusion may be into or out of the crack tip.
- (dp/dx) is negative for elastic behavior, so hydrogen goes to the crack tip.
- (dp/dx) is positive for plastic behavior, and the hydrogen is driven away from the crack tip.
- The maximum hydrogen concentration (as well as maximum triaxial stress) occurs at " χ_{cr} ," the elastic-plastic boundary.
- The large decrease in (da/dt) as tempering temperature increases is due to tempering effects on D_A (which could increase the number of traps or increase the ease of deformation at the crack tip).
- Suggests a grain by grain jump in cracking.

Further Work:

- Expand tempering range.
- Isolate effect of yield strength on diffusion.
- Examine the effect of " χ_{cr} " lying in the plastic zone instead of on the boundary. This may change the plot of (dp/dx) vs. (distance in front of crack), as well as other subsequent developments.

- Systematic studies of permeation on tempered and cold-worked tempered structures are required for the elucidation of the tempering- D_A relationship.
- Further work on the nature of the actual fracture mechanism is needed.
- Investigate the effect of "crack branching" on Stage II kinetics.

Critique:

- Tempering to obtain desired yield strength levels may have also affected other diffusion-limiting factors (such as grain size, segregation of impurities).
- Recent analyses have shown that " X_{cr} " would lie in the plastic zone, and not at the boundary. This may well change the present theoretical developments which depend on X_{cr} existing at the boundary of the elastic-plastic regions.
- The correlation between actual data and theoretical calculations is achieved mainly by the choice of the concentration-diffusivity term.
- The effect of tempering on D_A is only speculative.
- The overall understanding of the diffusivity and the actual fracture mechanism is lacking.

5. Gerberich and Chen (44) - 1975

Summary:

- Proposes that $K_{appl} = K_{Th}$ when the equilibrium concentration reaches a critical level.

Conclusions:

- The controlling mechanism is a critical concentration of hydrogen, its propensity to form being governed by yield strength, C_0 , state of stress, and temperature.
- $K_{Th} = f$ (hydrogen concentration)
- Hydrogen builds up around dislocations.
- $K_{appl} = K_{Th} \Big|_{C_{eq} = C_{cr}}$
- $K_{appl} > K_{Th} \Big|_{C_{eq} > C_{cr}}$ cracks.
- $K_{appl} < K_{Th} \Big|_{C_{eq} < C_{cr}}$ no cracking.

Further Work:

- Study effects of concentration on K_{Th} . Compare data to calculations.
- Investigate electrochemical and concentration gradient effects.
- Method needed to evaluate C_{cr} for different materials and conditions.

Critique:

- Model does not include electrochemical or concentration gradient effects.
- Little data on the concentration dependence of K_{Th} exists to compare to theoretical results.
- Critical concentration of hydrogen not given.
- What factors affect C_{cr} ?

6. Wanhill and van Leeuwen (45) - 1978

Summary:

- Applied fracture mechanics to ambient temperature sustained load fracture in structural materials.
- Ratio Analysis Diagrams (RADs) interpret the fracture resistance of materials in terms of damage-tolerant design. RADs are based on the correlation between K_{IC} and dynamic tear energy as functions of yield strength, and have been modified to include stress corrosion resistance and sustained load cracking resistance of titanium alloys.
- The high ratio region is where high stresses and large cracks are necessary to cause fast fracture or SCC. The low ratio region is where fast fracture or SCC can initiate from very small defects at moderate to low stress levels.

Conclusions:

- The most important and widespread failure mode in ambient temperature sustained load fracture is stress corrosion cracking.
- $K_{I_{Th}}$ should not be considered a material property, since it can depend on measurement sensitivity, the material, the environment, temperature, stress-state, and cutoff time.
- The time to failure consists of an incubation time and period of subcritical crack growth.
- The incubation time depends on $K_{I_{initial}}$ and prior history.
- Period for subcritical crack growth depends on specimen configuration and type of loading and the crack growth kinetics.

- Cracking in Regions I and III is strongly dependent on stress intensity. Crack velocity in Region II is independent of stress intensity.
- $K_{I_{Th}}$ should not be used as a design parameter because its long-range significance for service performance has not been established.
- $K_{I_{Th}}$ values do not necessarily provide safe levels of stress for all crack sizes.
- At low stress intensities and extremely low growth rates a true $K_{I_{SCC}}$ for aluminum alloys has not been observed.
- SCC can occur below " $K_{I_{SCC}}$ " in specimens with very small flaws or no apparent flaws because other forms of corrosion can occur, thereby providing stress risers that could increase the effective stress intensity to levels sufficiently high to cause eventual failure.
- Determination of inspection intervals based on Region II crack growth rates will be difficult or virtually impossible if the component geometry is complex, if stresses are relaxed as the crack grows, and if stresses are redistributed owing to permanent displacement changes under service loads (e.g. slip of bolted or riveted joints).

Further Work:

- Elucidation of the underlying mechanism of sustained load fracture.
- Development of a valid fracture parameter for materials selection.

- Development of reliable and reproducible tests for the above valid parameter.

7. Stepanov, et al (46) - 1979

Conclusions:

- Small change in stress gives large change in endurance time.
- There exists an activation energy for cracking.
- At cyclic loading, the failure probability for a given time must be greater than that at static loading.
- Cyclic failure can be probable at such low stress levels that static failure will not occur.

Critique:

- Large spread in data points--poor correlation.
- No proof of the accuracy or validity of various mathematical relationships.
- Difficult to measure some of the parameters in the endurance equations.

8. Nakasa, Takai, and Kido (47) - 1977

Summary:

- Studied the effect of superposition of repeating load on incubation time and crack propagation rate.
- Measure crack length optically.
- Environmentally induced delayed failure under static load consists of:

- 1) The adsorption and the invasion of hydrogen atoms to the material.
- 2) The diffusion and concentration of hydrogen atoms to the triaxial tensile stress state region ahead of crack tip.

Conclusions:

- Incubation time increases as K decreases.
- No crack propagation below K_{Th} .
- Crack propagation destroys the protective film on the crack tip, and so lowers $K_{I_{SCC}}$.
- Incubation time and $K_{I_{SCC}}$ are markedly decreased by superposition of ΔK .
- Increases in the frequency of loading cause decreases in incubation time.
- Crack propagation rate in delayed failure under repeating load is smaller than that under static load and larger than the fatigue crack propagation rate (CPR) in air.
- Crack propagation rate in delayed failure under repeating load cannot be estimated from those under static load.
- Fatigue crack propagation rate in corrosive environment cannot be expressed by a simple summation of both the fatigue crack propagation rate in air and the rate in delayed failure under static load.
- When ΔK and frequency of loading are large (and the incubation time or the CPR in water is similar to that in air) the initiation of crack growth and propagation occur by the mixture of

fatigue and delayed failure. Otherwise, crack growth and propagation are controlled by delayed failure alone.

- Repeating load destroys the oxide film, and so facilitates the adsorption of hydrogen atoms into the material.
- Repeating load generates the compressive retained stress or the microstructural change below the notch root which suppresses or facilitates the initiation of crack growth in delayed failure.
- Repeating load changes the position of the region with triaxial stress cyclicly, disturbing the concentration of hydrogen atoms to the region, and delays the occurrence of HAC.

$$\frac{da}{dt}_{\text{cyclic}} < \frac{da}{dt}_{\text{static}}$$

Further Work:

- An in-depth clarification is needed of the effects of repeating load on hydrogen adsorption mechanism.
- In what way does the compressive retained stress suppress the initiation of crack growth? Need data.
- Exactly how is the triaxial stress state changed under different loading conditions?

Critique:

- Optical measurement of crack length is prone to large error.
- Data correlation often poor.
- Many deductions made, and little proof given.
- Vague on the manner in which the triaxial stress state is changed during repeating load.

9. Boyer and Spurr (30) - 1978

Summary:

- Crack length in Ti-6Al-4V alloy monitored optically.
- Carried testing out to long times (500 days).
- Model based on hydride precipitation, where cracking takes place through creep, cleavage, or interfacial separation.
- Highest loaded specimens were the last to crack.

Conclusions:

- SLC of Ti-6Al-4V is significantly influenced by exposure temperature, hydrogen content, and basal plane crystallographic texture.
- Crack initiation and crack growth are independent of K (except that there exists a minimum stress intensity level required for cracking).
- Increasing hydrogen content raises the temperature at which SLC occurs and increases CGR (crack growth rate).
- Observed crack tunnelling.
- CGR below 0.1 mm/day stabilized; those above 0.1 mm/day continued growing.
- CGR increases as temperature decreases until it reaches a maximum, and then it decreases with decreasing temperature.
- Fracture is mixed mode.
- Above a critical temperature, nucleation of hydrides is the rate controlling mechanism. Below T_{Cr} , diffusion becomes the rate controlling mechanism.

Further Work:

- Study effects of temperature on CGR (extend testing range).
- Examine more closely the crystallographic influences on SLC.

Critique:

- Effect of temperature on CGR not given in detail.
- Need a larger range of testing temperatures.
- Crystallographic effects not studied in depth.
- Optical monitoring of crack length may give large errors.

10. Simpson and Puls (33) - 1979

Summary:

- Studied Zr-2.5Mo.
- Measured crack velocity by the potential drop method.
- Determined hydrogen flux (dn/dt) from crack velocity. Related the two by making several assumptions.
- Resolved "stepwise crack propagation" problem by formulating a "hinged hydride" model.
- Critical length for hinged hydride rupture is assumed to be equal to the striation spacing on the fracture surface.
- Used an average K for the period of measurement.
- Critical hydride length is strongly temperature dependent.
- 24 hours set as crack-arrest criterion.

Conclusions:

- Found a two-stage (da/dt) vs. K relationship independent of temperature.

- Formation of zirconium hydrides result in embrittlement and crack nucleation. The stress field at the crack tip is then capable of restarting the process, giving rise to stepwise crack propagation.
- Determined flux of hydrogen atoms to the stressed crack tip as a function of K , T , and hydrogen concentration.
- Driving force is the difference in local hydrogen concentration between hydride platelets close to and remote from the crack tip.
- This boundary condition is dominant due to large (14-17%) volume expansion accompanying hydride precipitation.
- The solubility of hydrogen in the material must be exceeded for this mechanism to take place.
- Solubility is 1 mg/g at 20°C; this rises exponentially to 60 mg/g at 300°C.
- Stage I: velocity increases strongly with K once K_{Th} was exceeded.
- Stage II: velocity is weakly K dependent.
- K_{Th} increases with temperature.
- Elastic crack tip stress field controls Stage I diffusion, and plastic zone stresses control Stage II.
- Elastic constraints play an important role in controlling the rate of hydrogen diffusion to the crack tip.
- Bulk hydrides dissolve before the crack tip hydrides, and so supply a source of hydrogen.

Further Work:

- Investigate "stepwise propagation" more thoroughly, and refine "hinged hydride" model.
- Determine accurately "K" at transition point and activation energy.
- What is the role of hydrogen content?
- Increase reproducibility of data.
- Explain why approaching test temperature from below gives very poor results, while approaching temperature from above gives better correlations.
- Study hydride microstructure and deformation mechanisms.

Critique:

- Assumes continuous propagation, which does not account for the stepwise nature of crack propagation.
- Crack velocity-hydrogen flux relationship is dependent on several assumptions--some of which are shown to be false.
- Experimental uncertainty in determining the value of K at the transition point.
- Model does not predict a threshold stress intensity.
- Much scatter in K_{TH} data--poor test-to-test correlations.
- Activation energy has a 25% error margin.
- Little is understood about the role of hydrogen content, except that the solubility limit must be exceeded for cracking.

- Only obtained reproducible values by approaching test temperatures from above. Approaching test temperature from below gave very poor results. This is not explained.
- Have insufficient information on the deformation mechanism for hydrides and on hydride microstructure.

11. Moody and Gerberich (22) - 1980

Summary:

- Studied Ti-6Al-6V-2Sn.
- Examined effects of hydrogen and temperature on K_{Th} .
- Define a $K_{effective}$.
- Used modified Dugdale-Baronblatt equation to relate $K_{effective}$ to $K_{applied}$.

Conclusions:

- K_{Th} drops slightly as temperature drops from 300°K (diffusion control).
- K_{Th} increases significantly with decreasing T above 300°K (Hydride nucleation problem).
- $CGR \propto \exp(k)$.
- Microstructure has a strong influence on K_{Th} . Hydrides form on specific crystallographic planes.
- Crack growth exhibits a three-stage dependency on $K_{applied}$.
- Near K_{Th} , CGR depends on both K and temperature.
- Average "semicohesive zone" width $\cong 40 \mu m$. This is the crack front region.

- As K increases to values just above K_{Th} , CGR accelerate rapidly. Extensive cleavage is found here.
- Rate limiting step is unresolved for α/β alloys.
- Below 300°K, the diffusion through the β matrix is the rate limiting step (from activation energy considerations).
- Maximum CGR is at 300°K.
- Above 300°K, diffusion through the β matrix no longer controls cracking rate--another unspecified factor or process governs HE at higher temperatures.

Further Work:

- Study of the "nucleation problem" for hydrides at $T > 300^\circ\text{K}$.
- Study of the "factor or process" that governs HE at $T > 300^\circ\text{K}$.
Study transition area where nucleation-diffusion factors control rate.
- Study HE processes at temperatures above 320°K.

Critique:

- Does temperature directly affect K_{Th} , or does temperature influence yield stress and other material parameters, which in turn affect K_{Th} ?
- Does not elaborate on the "nucleation problem" above 300°K.
- What is the "factor or process" which governs HE above 300°K?
- What happens in the transition area (at $\sim 300^\circ\text{K}$) where diffusion control gives way to nucleation of hydrides as the rate limiting step?

- Use higher temperatures to see if yet another process controls HE at very high temperatures.

12. Akhurst and Baker (48) - 1981

Summary:

- Transient crack growth is observed following load increases just below K_{Th} .
- Studied behavior of a tempered martensitic steel (3.5 NiCrMoV) in gaseous hydrogen.
- Prior γ grain size is ASTM #4.
- Crack length was measured by the back-face strain technique of Deans and Richards. Sensitive to ≈ 0.025 mm.
- Temperature range for testing was 25-80°C at 307 KPa hydrogen pressure.
- Pressure range was 169-514 KPa at 25°C.
- Crack arrest is defined as no growth for a period of 30 minutes.
- Assumes hydrogen concentration has no effect on flow stress.
- Model assumes: equilibrium levels of hydrogen are present beneath the crack tip at K_{Th} .
- This hydrogen reduces the critical load fracture stress in proportion to its concentration; this fracture stress must be exceeded over a critical distance.

Conclusions:

- Crack advances by the repeated nucleation of microcracks just ahead of the main crack.
- K_{Th} increases as temperature is increased or the pressure decreased.
- Crack fronts were relatively straight.
- Fracture was predominantly transgranular (some intergranular fracture also observed).
- Discontinuous cracking found by acoustic emission techniques.
- Maximum stress (and highest hydrogen concentration) is some distance in front of the crack tip.
- Hydrogen may be carried on moving dislocations resulting in concentrations above equilibrium levels at sites in the metal which block dislocation motion. This can lead to cracking at stress intensities below, but close to, K_{Th} . This cracking will not be sustained without an increase in load.
- K_{Th} increases with increasing temperature.
- K_{Th} decreases with increasing hydrogen pressure.
- The critical distance for HAC is considered to be constant for a given steel in a given condition.
- Crack path is often associated with prior γ grain boundaries, inclusions, lath boundaries.

Further Work:

- Study of environmental influences on K_{Th} .
- Study of the processes which control HAC.
- Study of factors which may affect the critical distance for HAC.
- Development of techniques for measuring material variables used in equation 11 of the paper.

Critique:

- Little discussion on environmental influences on K_{Th} .
- Is the critical distance for hydrogen induced cracking really a material property?
- Many parameters in the equation relating critical stress for fracture to hydrogen pressure (eq. 11) cannot be measured experimentally.
- Difficult to gauge the influence of temperature on K_{Th} with this model, since some of the material parameters are also temperature dependent.
- Is flow stress truly independent of hydrogen concentration?
- Can you alter one material parameter independently of the others?
- Lack of tests to determine material parameters leads to difficulty in comparing calculated and experimental approaches to check validity of model.

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