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NON-STEADY-STATE CRACK GROWTH BEHAVIOR OF AISI 4340 STEEL IN 3.5% SODIUM CHLORIDE SOLUTION

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NON-STEADY-STATE CRACK GROWTH BEHAVIOR OF AISI 4340 STEEL IN 3.5% SODIUM CHLORIDE SOLUTION

A DISSERTATION

Presented in Partial Fulfillment of the Requirements
the Degree of Doctor of Philosophy

By

Henry Wei-Ming Chung, M.S.
The Ohio State University
1983

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Approved by
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Department of Metallurgical Engineering
DEDICATION

TO MY PARENTS
ACKNOWLEDGEMENTS

I acknowledge the guidance and the assistance of Professor Digby D. Macdonald, my adviser, during the course of this research.

My thanks also go to Dr. Gustavo Cragnolino for his interest and suggestions. I would like to thank my wife Hui-Sheng Lee for her encouragement and support during the years of graduate study.

Mr. Wesley L. Page and Mr. Lennart T. Claussen of Civil Machine Shop are gratefully appreciated for their assistance for the preparation of the specimens. My thanks are also extended to Mr. Roland V. Farrar for his assistance with the electron microscopy, and Mr. Don Muilfield for his help in electronics.

Finally, financial support for this research by the Electric Power Research Institute, Dr. Michael Fox, Project Manager, under Contract No. RP1161-1, is gratefully acknowledged.
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"Steady and Non-steady Crack Growth Under Environmental Conditions," Paper to be presented at 16th ASTM symposium on fracture mechanics, Battelle Memorial Institute, Columbus, Ohio, August, 1983.
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Chapter I
INTRODUCTION

Among all the failure phenomena of engineering materials, stress corrosion cracking (SCC) and corrosion fatigue (CF) are most insidious. Failures due to stress corrosion and corrosion fatigue result from subcritical crack growth through engineering components. The occurrence of stress corrosion and corrosion fatigue requires a favorable metallurgical condition, and the conjoint action of environment and stress state. The difference between the two is the stress state. In an aggressive environment, failures result from stress corrosion cracking if sustained loads are employed; failures occur by corrosion fatigue if the material is under dynamic stresses. It has been suggested that these two phenomena are intimately related; stress corrosion may be a special low frequency (or strain rate) limiting case of corrosion fatigue (123). Accordingly, the same mechanisms may be operative for stress corrosion cracking and corrosion fatigue in any given material/environment system (1).
Efforts have been made to correlate the crack growth behaviors of stress corrosion cracking and corrosion fatigue because any correlation between these two phenomena is of obvious technological and fundamental importance. Many models have been proposed for the purpose of the establishment of this correlation (1,2). They generally can be classified into two categories: the superposition model (1) and the process competition model (2). These two models have worked successfully, to the first approximation, for several material/environment systems (1,2). However, it has been assumed in these models that stress corrosion cracking and fatigue are two separate failure mechanisms. The contribution of stress corrosion to corrosion fatigue can be directly obtained from the data obtained from stress corrosion cracking studies. It has been ignored that the stress corrosion cracking is not only a function of the stress state at the crack tip; but that it also depends on the loading history (22,26).

It is the purpose of this study to understand the stress corrosion crack growth response to different loading histories. The study was started with simple loading histories; and finally the stress corrosion crack growth behavior under dynamic stresses (dynamic stress corrosion cracking) was studied. Although it is difficult to
distinguish the difference between dynamic stress corrosion and corrosion fatigue, it can possibly be achieved under the conditions that stress corrosion crack growth rates are much higher than the fatigue crack growth rates in an inert environment. It is the situation when the stress amplitudes are small and the frequencies of dynamic stress are low.

The material/environment chosen for this study was high strength AISI 4340 steel (200 C temper) and 3.5% sodium chloride solutions. There were several reasons for selecting this system for this study. First, being an important engineering alloy, AISI 4340 steel is permeated with severe stress corrosion and corrosion fatigue problems to be solved. Second, the system has been extensively studied. Available experimental results show that dynamic stress corrosion conditions can be obtained in this system. Further, the failure mechanism of this system is relatively understood.
Chapter II
LITERATURE REVIEW

2.1 REVIEW OF LINEAR ELASTIC FRACTURE MECHANICS

2.1.1 Introduction

Stress corrosion cracking studies often made use of smooth specimens which were stressed in different hostile environments. Here the studies involved both the crack initiation and propagation stages. The major difficulty confronted by this kind of study had been the isolation of mechanisms of both stages since the crack propagated once it was initiated. Further, these studies had ignored the pre-existence of imperfections and flaws in engineering materials. In reflecting this fact, attention has been devoted to the study of crack propagation in recent years.

Today the mathematical tool employed by scientists and engineers to study the crack propagation is linear elastic
fracture mechanics (LEFM), by which a parameter, the stress intensity, $K$, has been established to characterize the mechanical driving force for crack propagation. In the past two decades, linear elastic fracture mechanics has been applied successfully to the study of subcritical crack growth in high strength steels, aluminum alloys, and titanium alloys. In general, such studies have involved determining the effect of stress intensity on the crack growth rate. This approach has made notable advances in understanding the mechanism and kinetics of stress corrosion cracking and has developed quantitative correlations between stress intensity and crack growth rate useful in the design of engineering components.

2.1.2 Griffith's Crack Theory

The quantitative relationships that engineers and scientists use today in determining the fracture of cracked solids were initially stated some fifty years ago by Griffith (3). Griffith noted that when a crack is introduced to a stressed plate of elastic material, a balance must be struck between the decrease in potential energy and the increase in surface energy resulting from the presence of the crack. Likewise, an existing crack
would grow by some increment if the necessary additional surface energy were supplied by the system. This surface energy arises from the fact that there is a nonequilibrium configuration of nearest neighbor atoms at any surface in a solid.

It is important to recognize that the Griffith relationship was derived for an elastic material containing a very sharp crack. As such the Griffith relationship should be considered necessary but not sufficient for failure. The crack tip radius also would have to be atomically sharp to raise the local stress above the cohesive strength. The Griffith relationship was confirmed by the study of the cracking of soda lime silica glass (3).

2.1.3 The Modes of Loading

A crack in a solid can be stressed in three different modes, as illustrated in Figure 1. Normal stresses give rise to the "opening mode" denoted as mode I. The displacement of the crack surfaces are perpendicular to the crack plane. In-plane shear results in "sliding mode" or mode II, in which the displacement of the crack surfaces is in the crack plane and perpendicular to the leading edge of the crack. The "tearing mode" or mode III is resulted
Figure 1 The basic modes of loading.
by out-of-plane shear. Crack surface displacements are in the crack plane and parallel to the leading edge of the crack. Mode I loading is encountered in the majority of practical engineering situations involving cracked components. Mode II is found less frequently. Mode III may be regarded as a pure shear problem such as that involving a notched round bar in torsion.

2.1.4 Energy Release Rate Analysis

For an elastically loaded body containing a crack of length a (Figure 2), the amount of stored elastic strain energy is given by $U = \frac{1}{2}P\cdot$ where $U$ is the elastic stored energy, $P$ is the applied load, and $\cdot$ is the displacement. In the case of Mode I loading, $\cdot$ can be replaced by $CP$ where $C$ is the compliance of the solid. For a small increment of $da$, the necessary additional surface energy is obtained from the work done by the external body forces $Pd\cdot$ and the release of strain energy $dV$. As a result

$$\frac{dU}{da} = \gamma = P \frac{d\sigma}{da} - \frac{dV}{da} \quad (1)$$
Figure 2 Load-deflection response of cracked plate.
with the compliance of the body increases. It can be shown that under either fixed load or fixed displacement conditions, the rate of change of the potential energy per unit increment of the crack length follows that

\[ \dot{G} = \frac{dU}{da} = \frac{P^2}{2} \frac{\partial C}{\partial a} \]  

(2)

for the plate of unit thickness. At the instability, then, the critical strain energy release rate is

\[ \dot{G}_c = \frac{P_{\text{max}}^2}{2} \frac{\partial C}{\partial a} \]  

(3)

Once the compliance versus crack length relationship has been established for a given specimen configuration, \( G_c \) can be obtained by noting the load at fracture, provided the amount of plastic deformation at the crack tip is kept to a minimum.
2.1.5 **Stress Analysis**

The fracture of cracked solid can also be analyzed by stress analysis in terms of linear elastic theory. By assuming Airy stress functions to the equilibrium and compatibility requirements for various sample configuration and stress patterns, Westergaard (4) was able to determine the nature of the crack tip stress distributions. For the notations shown in Figure 3, the crack tip stress distributions are found to be, for Mode I loading,

\[
\begin{align*}
\sigma_x &= \frac{K_I}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \left[1 - \sin \frac{\theta}{2} \sin \frac{3\theta}{2}\right] \\
\sigma_y &= \frac{K_I}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \left[1 + \sin \frac{\theta}{2} \sin \frac{3\theta}{2}\right] \\
\tau_{xy} &= \frac{K_I}{\sqrt{2\pi r}} \sin \frac{\theta}{2} \cos \frac{\theta}{2} \cos \frac{3\theta}{2}
\end{align*}
\]

For plane strain, \( \sigma_z = 0 \); for plane stress \( \sigma_z = \nu(\sigma_x + \sigma_y) \), where \( \nu \) is Poisson ratio. For an infinite cracked solid with uniform uniaxial tension at infinity

\[ K_I = \sigma \sqrt{\pi a} \]  

(5)

For mode II loading, the stress distributions are

\[
\begin{align*}
\sigma_x &= -\frac{K_{II}}{\sqrt{2\pi r}} \sin \frac{\theta}{2} \left[2 + \cos \frac{\theta}{2} \cos \frac{3\theta}{2}\right] \\
\sigma_y &= \frac{K_{II}}{\sqrt{2\pi r}} \sin \frac{\theta}{2} \cos \frac{\theta}{2} \cos \frac{3\theta}{2} \\
\tau_{xy} &= \frac{K_{II}}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \left[1 - \sin \frac{\theta}{2} \sin \frac{3\theta}{2}\right] \\
\sigma_z &= \nu(\sigma_x + \sigma_y), \quad \tau_{xz} = \tau_{yz} = 0
\end{align*}
\]

(6)
Figure 3 Distribution of stresses in vicinity of crack tip.
For an infinite cracked solid with uniform in-plane shear at infinity,

\[ K_I = \frac{\gamma}{\pi a} \]  

(8)

and similarly for mode III loading

\[ \gamma_{I I} = -\frac{K_{I I}}{2\pi} \sin \frac{\theta}{2} \]

\[ \gamma_{I I} = \frac{K_{I I}}{2\pi} \cos \frac{\theta}{2} \]  

(9)

\[ \sigma_x = \sigma_y = \sigma_z = \tau_{xy} = 0 \]  

(10)

An important feature of these equations is that the stress distribution around a sharp crack tip is similar and depends only on \( r \) and \( \theta \). The difference between one cracked component and another is simply the magnitude of \( K \). In essence, \( K \), which is defined as stress intensity factor, serves as a mechanical parameter to define the crack tip stress field. In practice, for finite-sized samples, the stress intensity factor \( K \) is also a function of the geometry of the sample. It has been shown by Irwin (5) that the stress intensity factor, \( K \), related to the strain rate release rate, \( \dot{\gamma} \), by

\[ K = \sqrt{\frac{E \dot{\gamma}}{\pi}} \quad (\text{plane stress}) \]  

(11)

\[ K = \sqrt{\frac{E \dot{\gamma}}{2(1-\nu^2)}} \quad (\text{plane strain}) \]  

(12)
where $E$ is the Young's modulus of the material. When $\frac{K}{c} = K_c$, the corresponding $K$ is fracture toughness, $K_c$.

2.1.6 The Crack Tip Plastic Zone

It is apparent from Equations (4, 6, 10) the local stress may rise steeply as $r$ approaches zero. This circumstance is, however, precluded by the onset of plastic deformation at the crack tip. A first approximation of the size of the plastic zone can be obtained by determining the maximum value of $r$, in Equations (4, 6, 10), produces the elastic stress exceeding the yield strength. The plastic zone size ahead of the crack tip calculated by this method is $K^2/2\pi \sigma_y^2$. In fact, the plastic zone size is little larger than this value as a result of load redistributions around the plastic zone. McClintock and Irwin (6) have found that for plane stress the size of the plastic zone is approximately twice of that value. Therefore

$$
\gamma \sim \frac{1}{2\pi} \frac{K^2}{\sigma_y^2} \quad (13)
$$
For plane strain where the triaxial stress field suppresses the plastic zone, the size of the plastic zone is smaller and has been estimated to be

$$r_j \approx \frac{1}{6\pi} \frac{K^2}{\sigma_y^2}$$ \hspace{1cm} (14)

In Irwin's approach, a uniform yield strength throughout the plastic zone has been assumed. However, more accurate analyses have showed that the stress distribution within the plastic zone is more complex.

2.1.7 Stress Distribution in the Plastic Zone

Consider how the maximum transverse principal stress in the region around a crack tip in a stressed solid varies with successive increment of nominal stress $\sigma_{nom}$. Initially the solid remains elastic, and the maximum value stress, $\sigma_{max}$, is given by Inglis solution (7),

$$\sigma_{max} = \sigma_{nom} \left(1 + 2\sqrt{\frac{a}{\rho}}\right)$$ \hspace{1cm} (15)
where \( p \) is the crack tip radius. If the crack tip is sharp, \( p \) is few micrometers and the stress intensification factor could easily be one hundred. Therefore, \( \sigma_{\text{max}} \) rises steeply with small increment of \( \sigma_{\text{nom}} \). When \( \sigma_{\text{max}} \) reaches the yield strength, \( \sigma_y \), a plastic zone forms at the crack tip, and \( \sigma_{\text{nom}} \) is limited by this value at the free surface. Upon further increase in \( \sigma_{\text{nom}} \), the plastic zone grows larger; \( \sigma_{\text{max}} \) rises steeply beyond the crack tip due to surrounding elastic region, and it passes a maximum at some distance ahead of the crack tip. Finally, \( \sigma_{\text{max}} \) reaches its limiting value. Rich and Johnson (8-10) has calculated the stress distribution ahead of a crack tip, assuming plane strain and small scale yielding. Their results for a Mises material and a strain-hardening material with the hardening exponent \( n = 0.1 \) are shown in Figure 4. They have found that the limiting value of \( \sigma_{\text{max}} \) is about \( 3 \sigma_y \), and the position of \( \sigma_{\text{max}} \) is at a distance of twice of the crack tip opening displacement, \( 2 \delta_t \), from the crack tip. The relationship between \( \delta_t \) and \( K \) can be given by (11)

\[
\delta_t \approx \frac{1}{2} \frac{K^2}{E \sigma_y} \tag{16}
\]
Figure 4 Stress distribution in vicinity of a sharp crack tip.
The crack tip stress field obtained by continuum mechanics can be correlated to linear elastic fracture mechanics. When $K$ is low, small increments in $K$ increase both $\sigma_{\max}$ and the size of the plastic zone, and the region of $\sigma_{\max}$ is shifted further away from the crack tip. When $3 \sigma_{YS}$ is attained, further increase in $K$, the stress distribution simply spread over a wider region along with an increase in the size of the plastic zone and the shift of the region of $\sigma_{\max}$. The variation of hydrostatic tension with nominal stress, $\sigma_{nom}$, is similar to $\sigma_{\max}$, Figure 5. The maximum hydrostatic tension is in the same region of $\sigma_{\max}$.

2.1.8 Specimen Geometries

Precracked specimens are classified with respect to the relationship between the stress intensity factor $K$ and crack extension, Figure 6 (12). Depending on the method of stressing and/or the geometry of the specimen, the fracture mechanics specimens may be divided into three categories:

1. Increasing $K$ specimens.
2. Decreasing $K$ specimens.
3. Constant $K$ specimens.
Figure 5 Schematic representation of maximum principal stress in region of crack tip at successively higher loading increments.
Figure 6 Classification of precracked specimens for stress corrosion crack testing.
In the first category of precracked specimen configurations, specimens are usually stressed under constant load conditions in tension. In addition, a classification is made between these specimens loaded to the precrack (crackline loaded) and at a distance from the precrack (remote loaded). Single-edge-cracked plate specimens are classified according to the proximity of the boundary normal to the direction of the crack plane, the crack tip stress field being either affected (w-a dominated) or unaffected (w-a indifferent) by this boundary, where w is the length of the specimen measured alone the lines of load application.

In the second category of precrack specimen configurations, specimens can be stressed under conditions of constant deflection or constant load. Crackline-loaded single-edge-cracked plate specimens are maintained at constant crack-opening displacement (measured along the lines of load application) by a bolt, wedge, or other devices. The overall result of this procedure is to cause the load to reduce and, consequently, the K to decrease as the crack extends under the influence of an aggressive environment.
Typical crackline-loaded specimens are double cantilever beam (w-a indifferent, DCB), and wedge-opening load (w-a dominated WOL) specimens. Some examples of these specimens are shown in Figure 7. Double cantilever beam and wedge-opening load specimens can be used in either increasing or decreasing $K$ tests on plate materials. However, double cantilever beam specimens have often been used in decreasing $K$ test, and wedge-opening load specimens have often been used in increasing $K$ test.

In the third category of precracked specimens, a linear relationship between specimen compliance and crack length is obtained to produce constant $K$ with crack extension over several centimeters. The constant $K$ specimens, which are also called contoured double cantilever beam (contoured DCB) specimens, have often been employed for fundamental studies of subcritical crack growth because the independence of $K$ on crack extension enables researchers to control the history of stress intensity on the test piece. Two examples are shown in Figure 8.
Figure 7 Configurations of DCB and WOL plate specimens.
Figure 8 Configurations of constant $K_I$ specimen.
2.1.9 Side Grooving

Investigators using crackline-loaded specimens in particular have experienced difficulty in restricting cracking to deviate from the plane of the machined notch. Crack bifurcation or macrobranches can be prevented by providing the specimens with side grooves along the crackline (14,15). Side grooves have also been applied to suppress the formation of shear lips and to enhance plane strain (16,17) and straighten crack front. Limiting the size of shear lip facilitates the direct observation of crack length. It has been noticed (18) that the correction factor in $K_I$ for shallow, angular side grooves takes the expected form of $(B/B_N)^m$, where $B$ and $B_N$ are full- and grooved-reduced thickness, respectively, and where $0.5 < m < 1$. Nevertheless the influence of side grooving on the stress intensity factor is far from established, and correction factors should be treated with caution, especially if deep side grooves are used.
2.2 STRESS CORROSION CRACKING OF AISI 4340 STEEL IN DISTILLED WATER AND SEA WATER

2.2.1 General Characteristics

Application of fracture mechanics techniques to the environment assisted subcritical crack growth of AISI 4340 steel in hydrogen-containing environments has shown that the subcritical crack growth response may be separated into three stages, Figure 9 (19,20). At low value of $K_I$ the crack growth rate ($\frac{da}{dt}$) is strongly dependent on $K$ and becomes negligible as a threshold stress intensity, $K_{th}$, or $K_{SCC}$ in cases of stress corrosion cracking, is approached. This region of crack growth has been designated as Stage I. At intermediate value of $K_I$ crack growth rate becomes less dependent on $K_I$ (Stage II). As $K_I$ approaches the fracture toughness of the material, $K_{IC}$, crack growth rate increases rapidly and again becomes strongly dependent on $K_I$ (Stage III). Depending on mechanical parameters and microstructure of the material, Stage I and/or Stage II behaviors may be absent. Typical stress corrosion crack growth rate versus stress intensity correlation of AISI 4340 steel in distilled water is shown in Figure 10 (21).

The most important mechanical parameter affecting the crack growth response is the yield strength. $K_{ISCC}$ was found to have similar dependence as the fracture toughness.
Figure 9 Schematic of stress corrosion crack growth rate versus stress intensity.
Figure 10 Subcritical crack growth rate versus stress intensity of AISI 4340 Steel in distilled water.
on yield strength, i.e., both are reduced when the yield strength affects not only the resistance to stress corrosion cracking, it also affect the crack propagation. It has been found that the crack growth rate, at a given stress intensity level, increases when the material's yield strength is higher. It has been suggested that the crack growth behaviours of Stages I and III are mechanically controlled. However, the crack growth rate resulting from stress intensity level in the Stage II region was found to have an Arrhenius-type relationship with temperature and to exhibit an activation energy of about 38 kJ/mole, which is slightly dependent on applied stress intensity (22-24).

In studying crack propagation under stress corrosion conditions, it has been generally assumed that under constant environmental conditions, the crack growth rate depends only on the mechanical driving force for crack extension, $K_I$; and $(\frac{da}{dt})$ is invariant respect to time for constant $K_I$. This is must be true if $K$ is to be a proper representation of the mechanical driving force for crack extension, and is the case for steady-state crack growth. The correspondence, however, does not preclude the dependence of the crack growth on applied $K$. The existence of an incubation period for precracked specimens has been demonstrated by Benjamin and Steigerwald (25) on AISI 4340
steel tested in water. They showed that loading history could affect the incubation period. Testings conducted under constant load, decreasing K conditions showed that crack growth rate was dependent on stress intensity history (25).

Close examination of the crack growth response to a suddenly applied constant K revealed that crack growth rate did not achieve a steady-state value only until an incubation period of no crack extension and a transient period of time-dependent crack growth, Figure 11 (26,27). The study using DCB specimen also showed that the crack growth rates were function of the starting stress intensity, Figure 12 (26).

Extensive studies of stress corrosion cracking of AISI 4340 steel in distilled water and aqueous sodium chloride solutions have showed that the crack essentially propagates along the prior austenite grain boundaries (28-30). The intergranular cracking path has been related to the phenomena of microbranches (31) which have often been observed on the specimen along the crack plane of this kind of steel.
Figure 11 Crack growth response to the application of stress intensity.
Figure 12 Dependence of crack growth rate on the initial stress intensity.
2.2.2 **Effect of Composition**

Sandoz (32-34), in his comprehensive studies on the role of alloying elements in stress corrosion cracking of high-strength steel, found that increasing carbon from 0.15 to 0.53%, in AISI 4340 steel, significantly decreased stress corrosion cracking resistance, but only under open circuit conditions; he found no effect on $K_{isc}$ for cathodic and anodic polarization (32). The open-circuit data are shown in Figure 13(a); there is some uncertainty about the increase in stress corrosion cracking resistance beyond 0.4%C. It was suggested that the crack tip changed from anodic to cathodic condition with increasing carbon content (33,34). The deleterious effect of carbon has also been found by others (35-37).

The common substitutional additions to AISI 4340 steel are chromium, manganese, nickel, silicon, and molybdenum. There appears to be agreement that manganese increases susceptibility to stress corrosion cracking. It was shown by Sandoz (33) that an increase from 0.1 to 2.7%Mn in AISI 4340 steel resulted in a decrease in $K_{isc}$ in salt water for anodic, open-circuit, cathodic conditions (Figure 13(b)). It was suggested that the addition of manganese changed the
Figure 13 The effects of (a) carbon and (b) manganese on the stress corrosion cracking of AISI 4340 steels.
fracture behavior in AISI 4340 steel immersed in aqueous environments (33,38,39).

The beneficial effects of silicon is well documented. Carter examined silicon additions in AISI 4340 steels, and for a variety of strength levels, found general improvements up to Si additions in excess of 2% (40,41). At medium strength levels, improvement in stress corrosion cracking resistance resulted from the increase in Si contents at 0.5 to 1.0%, which was related to changes in tempering behavior. At high strength levels (about 2000 MPa), improved resistance came instead from the decrease in crack growth rate (Figure 14). It has been suggested that the effectiveness of Si is related to its abilities to prevent epsilon carbide from acting as a cathodic site for hydrogen discharge (40,41); that the carbide improves crack resistance by acting as a hydrogen trap (42); and that silicon reduces the diffusivity of deleterious species, such as hydrogen (38,43). Sandoz (32) has found that Si is beneficial through its effect in shifting stage III tempering to higher temperature and improving the resistance to one-step-temper embrittlement; however, Si is damaging when segregated to grain boundaries.
Figure 14 The effect of silicon on the stress corrosion resistance of AISI 4340 steels.
For a given strength level, it was found that the additions of chromium, nickel, cobalt, and molybdenum had almost no effects on the stress corrosion cracking resistance of AISI 4340 steel. Even the undesirable impurities, such as sulfur and phosphorus, did not reduce the crack resistance when their contents were increased (32-34).

Stress corrosion cracking of high-strength AISI 4340 steel in distilled water or sodium chloride aqueous solution has been attributed to hydrogen embrittlement (43-45). Effects of hydrogen on the stress corrosion resistance of AISI 4340 steel and fracture morphology have been shown to be closely related to the effects of temper embrittlement also promote by hydrogen cracking along prior austenite grain boundaries, and the transgranular fracture. In high-strength martensitic steel susceptible to temper embrittlement, decreased $K_{IC}$ are related to the tendency for cracking along prior austenite grain boundaries (21,47,48). P, S and other metalloids directly degrade prior austenite grain boundaries. Other elements which enhance adsorption of metalloids on grain boundaries also promote degradation. It has been shown that Mn and Si in solution and thus increase the chemical potential gradient driving diffusion of P and S to boundaries (49). The
effect of cracking is greatest when the amount of metalloid is a minimum, and vice versa, but there is an additive effect. However, temper embrittlement appears not necessary for hydrogen cracking (21). Simmons et al have studied the subcritical crack growth of ultrapure AISI 4340 steel in gaseous hydrogen, water vapor, and liquid water. For the tempering condition employed (204°C), the crack propagates along the prior austensite grain boundaries, where no segregation has been observed except the presence of carbide.

2.2.3 Effect of Melting Practice

Melting procedure was found to influence $K_{I_{SCC}}$ markedly, Figure 15 (32). AISI 4340 steel which has been vacuum-degassed during melting appears to have better resistance to crack growth in moist air than air-melted AISI 4340. Vacuum-arc-remelted 300M steel, a silicon-modified commercial 4340 steel is relatively also resistant to cracking in moist air. The difference in $K_{I_{SCC}}$ values between air-melted and vacuum-melted AISI 4340 steel and 300M steel was attributed to a lower impurity level, particularly the levels of P and S and other metalloids (32,33).
Figure 15 The effects of melting practice on the stress cracking resistance of commercial AISI 4340 steels tested in 90% humidity air.
2.2.4 **Effect of Heat Treatment and Microstructure**

Reviews of the early data, mostly on smooth specimens, show that the general trend is for SCC resistance to increase with higher tempering temperatures \((41,50,51)\). However, there is an intermediate tempering temperature range \((250 - 450^\circ C)\), in which AISI 4340 steels are more susceptible to SCC. This is so-called temper embrittlement. AISI 4340 steels tempered in this temperature range have been avoided in most delayed failure studies to reduce the complication arising from temper embrittlement.

The effects of tempering temperatures on AISI 4340 are obviously related to the resulting yield strength \((52,53)\). It has been suggested that the improvement with increasing tempering temperature, excluding the tempering temperature range of high susceptibility to temper embrittlement, results from progressively less epsilon carbide and more cementite in the microstructure \((54)\), but this suggestion has not been supported generally \((55)\). The distribution of carbides is also important \((56,58)\), untempered martensite is highly detrimental to SCC resistance \((57)\).
Since SCC in high strength steels is generally intergranular, it is obvious that the compositional variations and solid state reactions which take place at boundaries may be important. Martensite plate boundaries and transformation twins are known to be favorable nucleation sites for carbide precipitation (58) and hence may also provide preferential and easy paths for crack propagation.

Although stress corrosion cracks generally progress intergranularly, there are no large effects of grain size (59,60). An increase in ASTM grain size number from 7 to 12 increased the yield strength from 245 to 265 ksi, but the threshold stress intensity remained essentially the same.

2.3 THE CORROSION FATIGUE CRACK GROWTH BEHAVIOR

There are three basic types of corrosion fatigue crack growth behavior (61). They are true corrosion fatigue, stress corrosion fatigue, and the combination of the two. The threshold stress intensity in stress corrosion cracking provides an important separation point between these different types of crack growth behavior. True corrosion fatigue identifies the behavior where fatigue crack growth rates are enhanced by the presence of an aggressive
environment through a synergistic action of corrosion and cyclic loading. This is 'below Kiscc' behavior and applies to materials which do not stress corrode and that Kic = Kiscc (Figure 16(a)). True corrosion fatigue behavior is characterized by different values of C and n in the Paris equation, from those relevant to an inert environment. Stress corrosion fatigue presents the phenomenon of static load stress corrosion under fatigue conditions. This occurs whenever the stress intensity in the fatigue cycle is above Kiscc. This is 'above Kiscc' behavior. Stress corrosion fatigue behavior for materials which do not exhibit environmental enhancement until Kiscc is reached (Figure 16(b)) and is characterized by a 'bump' with a growth rate plateau as usually observed in stress corrosion crack growth. The most common type of behavior pertains to material/environment systems which exhibit stress corrosion fatigue above Kiscc and true corrosion fatigue throughout. Such behavior is shown in Figure 16(c).

2.3.1 The Superposition Model

It was suggested by Wei (62) that the mechanisms for moisture- and hydrogen-enhanced subcritical crack growth in high strength steels under sustained load and in fatigue may be the same on the basis of the fact that nearly all of
Figure 16 Three basic types of corrosion fatigue crack growth behavior.
The effects of water vapor and hydrogen on subcritical crack growth under sustained loads reported by Johnson and Willner (63) and Hancock and Johnson (64) were reproduced for fatigue (66,67). It has been observed that the fatigue crack growth rate in hydrogen depend strongly on the test frequency, whereas the rates of fatigue crack growth in argon are nearly independent of the test frequency; and that the form of the fatigue crack growth rate versus $K_{\max}$ curve is quite similar to the growth rate versus $K$ curve under sustained loads.

These results suggest that the observed frequency effect is the result of environment-enhanced crack growth rather than a reflection of the rate sensitivity of the material. Consequently, Wei and Landes suggested that it seems reasonable to consider fatigue crack growth in high strength steels in an aggressive environment to be composed of two components — a mechanical component and an environmental component — and to consider the corrosion fatigue crack growth rate, to a first order approximation, to be simply equal to the algebraic sum of the rates of the growth of these two components (1). The growth of these two components. The mechanical component represents the fatigue crack growth rate in the absence of the influence of an external environment and is determined experimentally
by testing in an inert environment or in vacuum. The environmental component is to be determined from experimental crack growth data under sustained loading in the appropriate environment and the fatigue load profile which would incorporate both the loading variables, and frequency.

Formally, the corrosion fatigue crack growth rate \((da/dN)_c\), is expressed in terms of fatigue crack growth rate in an inert reference environment, \((da/dN)_r\), and an environmental component, computed from sustained-load crack growth data obtained in an identical aggressive environment and the load profile represented by \(K(t)\),

\[
(da/dN)_c = (da/dN)_r + \int_{cycle} (da/dt) \times K(t) \ dt \quad (17)
\]

Integration is taken over one cycle of fatigue loading and incorporates the effects of frequency and loading variables through \(K(t)\).

Comparisons of the model with experimental data were fairly good for low \(R\) ratio; whereas, for high \(R\) ratios, the model tended to overestimate the corrosion fatigue crack growth rates. One implication of the superposition is that no environmental effect can be observed if the cyclic loadings do not give rise the stress intensity exceeding the
threshold stress corrosion stress intensity, \( K_{\text{ISC}} \). It is obviously contrary the fact.

2.3.2 The Process Competition Model

This model was proposed by Austen and Walker (67-69). The basis of the model is that the processes of stress corrosion and true corrosion fatigue are mutually competitive, not additive as in the Wei and Landes model. It has been assumed that the crack will propagate by the fastest available mechanism pertinent to the prevailing stress intensity.

In Austen and Walker's view, the Process Competition Model may be extended to account for the effects of cyclic waveform on stress corrosion fatigue. This can be done by assuming that the stress corrosion fatigue crack growth rate over the relevant \( K \) cycle is the average stress corrosion rate rather than the stress corrosion rate at the maximum stress intensity in the cycle. The Process Competition Model can, then, be used to predict corrosion fatigue crack growth rate behavior and consequently to determine corrosion fatigue lifetimes for any combination of stress ratio, frequency, and waveform.
In spite of the difference in the basic assumptions of the superposition and process competition models, it is required by both models to take into account of the crack growth rates resulting from the stress corrosion cracking under cyclic loadings. The same method was applied to calculate these crack growth rate. It was implicitly assumed that the stress corrosion cracking growth rate over a load cycle was the average of the stress corrosion cracking growth rate, obtained under sustained loading.

2.4 THE MECHANISMS OF STRESS CORROSION CRACKING

Hydrogen embrittlement is one of the models proposed to explain delayed failures of engineering materials in hostile environment. However, due to its particular importance to the present study; it was singled out from other proposed mechanisms of stress corrosion cracking, and is reviewed in the next two sections.

2.4.1 The Film Rupture Model

This model, also regarded by some researchers as slip-dissolution model (70,71), was originated by Champion (72) and Logan (73). The basic hypothesis is that a protective surface film at the crack tip is ruptured by localized
plastic deformation, permitting rapid dissolution of the exposed substrate while the non-deforming crack walls remain protected by film, Figure 17. The protective film is generally regarded to be passive and, therefore, the repassivation rate of the exposed surface is considered to be a determining factor as to a material's susceptibility to stress corrosion cracking.

In his original proposal, Champion suggested that anodic dissolution must provide sufficient stress concentration to trigger further plastic deformation, and accompanying film rupture before the exposed surface is completely repassivated, otherwise the material will be immune to cracking in this particular environment. Champion's approach indicated that the crack tip does not become completely repassivated, and that the crack advances continuously.

Staehle and Vermilyea (70,71,74,75), however, have proposed the alternative view that the crack tip becomes completely repassivated. Vermilyea suggests that the metal at the crack tip dissolves until repassivation is complete and the film ruptures as a result of creep, Figure 18 (74,75). Staehle (70,71) adopts that film rupture results from the emergence of slip steps through the
Figure 17 Schematic of film-rupture model.
Figure 18 Schematic of slip-dissolution model proposed by Staehle.
passive film. Burlse and Pugh (76) propose that the Champion's model, modified to include film rupture by the emergence of slip steps, can reasonably account for crack propagation in a passivating solution. Such a model, with the additional assumption that repassivation is slower at grain boundaries, is consistent with a number of fractographic observations for intergranular stress corrosion cracking, in which fracture surfaces are smooth and featureless, except for occasional slip steps.

2.4.2 The Tunnel Model

This model, first proposed by Swann and coworkers (77,78), suggests that fracturing is initiated at slip steps by the formation of arrays of fine corrosion tunnels which grow in length and diameter until the remaining ligments fail by ductile rupture, Figure 19. The crack is then thought to propagate discontinuously by repeating cycles of tunnel growth and ductile rupture. The model can only apply to transgranular stress corrosion cracking, and the fracture surface is expected to exhibit grooves extending in the direction of crack propagation, with the walls between neighboring grooves matching peak-to-peak on the opposited faces. Such fracture surface has been observed in one isolated case, that is, in an austenistic
Figure 19 Schematic of tunnel model.
stainless steel (18%Cr, 10%Ni) tested in a sulfuric acid-sodium chloride solution (79).

2.4.3 The Selective Dissolution Model

This model was proposed by Forty (80) to account for the transgranular stress corrosion cracking of alpha brass in aqueous ammoniacal solutions. It was based on the competition between brittle fracture and plastic deformation at stress concentrators. Forty suggested that the selective dissolution of zinc from the alloy results in vacancy injection which, in turn, sufficiently restricts local plastic deformation to permit the initiation of a cleavage crack. The crack was thought to propagate at high velocity without dislocation generation until it encounters a pre-existing slip band, at which arrest occurs by plastic blunting. Repeated cycles of this process were believed to lead to discontinuous cleavage cracking. However, as pointed out Bursle and Pugh (76), Forty's model fails to explain why other solutions, such as sea water, which cause dezincification, do not cause stress corrosion cracking.
2.4.4 The Tarnish Rupture Model

This model was initiated by Forty and Humble (81) to account for stress corrosion cracking of Cu-Zn alloys in aqueous ammonia, and was further developed by MeEvily and Bond (82). It has been observed that the grain boundaries in Cu-Zn alloys are penetrated by the thick tarnish film, and that, in the absence of stress, this preferential attack attains a limiting depth (83). The latter was attributed to growth becoming limited by transport across the film. In stressed material, the film was considered to undergo repeated rupture, thus destroying the transport barrier and permitting continued penetration of the boundary, Figure 20. Rupture of the brittle tarnish was attributed to elastic strains introduced by creep in the surrounding metal, following the approach of Vermilyea.

2.5 THE MECHANISMS OF HYDROGEN EMBRITTLEMENT

In the years since the role of hydrogen in reducing the ductility and/or the fracture strength of materials has been recognized, a variety of mechanisms has been proposed to account for the observations. These can be categorized into a few general classes as listed below:

1. decohesion
Figure 20 Schematic of tarnish rupture model.
2. surface adsorption effects
3. hydride precipitation
4. high pressure bubble formation
5. plastic deformation effects

Since factors such as hydrogen solubility, hydride stability, hydrogen diffusivity, etc. differ so widely among systems which are embrittled by hydrogen, no single failure mechanism can be identified to be responsible for failure in all systems. A brief review of proposed mechanisms is presented below with emphasis on those commonly accepted to be more suitable for the delayed failure of high strength steels.

2.5.1 The Decohesion Mechanisms

The concept of decohesion was first suggested by Troiano (84,85) and has recently been expanded by Oriani and Josephic (86-88). The basic hypothesis of the decohesion mechanism is that brittle fracture occurs when the local stress exceeds the atomic bond strength and that the presence of hydrogen as a solute decreases the atomic bond strength. In this model, the plastic deformation which precedes fracture and which occurs at the crack tip plays a role in the fracture process but does not lead to
hydrogen embrittlement itself. The deformation can affect the $K$ at the crack tip, may influence the rate of hydrogen transport to the crack or may influence the fracture process in other ways. In this sense, failure by decohesion is competitive with ductile rupture mechanisms. It is noted that decohesion mechanism can take place in conjunction with general plasticity in the solid as well as with local deformation at the crack tip. Thomson and Rice (89) have discussed the possibility of the formation of an atomically sharp crack shielded by a plastic zone. Although the calculation is highly idealized and uses Hookean elastic elements to model the atomic interaction, they show that under the condition that the activation energy for spontaneous dislocation loop generation at the crack tip is greater than zero, the crack tip may remain atomically sharp despite the presence of a plastic zone around the crack.

The decohesion mechanism postulates that hydrogen makes a decrease in the maximum bonding strength between atoms across an atomic plane as they are being reversibly separated. The basic assumption is, therefore, that brittle fracture occurs over a critical distance, at which the local applied stress exceeds cohesive strength. The variation of cohesive strength and the critical distance
with hydrogen is not known, but it is assumed that cohesive strength decreases as the local hydrogen concentration is increased.

In homogeneous elastic solid the decohesion mechanism would result in continuous crack propagation by bond breaking at the crack tip. Sonic emissions accompany the advance of a crack in a hydrogen embrittled steel (88,90) indicating that the crack advance is in fact discontinuous. In a real material this would be expected due to structural inhomogeneities and the plasticity which accompanies fracture in a material such as steel. Hydrogen assisted bond breaking could be expected both at the crack tip and at points in advance of the crack front at which particularly high stress existed because of the crack tip plastic deformation or at which second phase interfaces existed.

2.5.2 Surface Energy

Petch and Stables proposed that the crack formed in accordance with the Griffith fracture model, and hydrogen adsorption could reduce the surface energy of the surfaces created in crack growth (91,92). There are several objections against the model. The effective surface energy
is, in general, much greater than the thermodynamic surface energy and should include the energy of plastic deformation which is present in crack growth. Hydrogen adsorption can reduce thermodynamic surface energy, but the energy of plastic deformation is hardly affected. Oxygen, which has a greater heat of adsorption than hydrogen, however, can decrease hydrogen embrittlement rather than promoting it.

Further, based on the surface adsorption mechanism, the crack growth rate at given $K_i$ is expected to decrease with increasing temperature; however, such an implication contradicts the experimental observations below 273K (93,94). The model also fails to predict the discontinuous crack growth in high strength steels and, neither can the model explain the initiation of microcrack ahead of the crack in the region of maximum hydrostatic tension. Further, reversibility of delayed failure upon releasing stress cannot be accounted for by the model.

### 2.5.3 Hydride Formation

Many metals which exhibit severe hydrogen embrittlement are also known to form hydrides. In Group Vb metals and Zr alloys, precipitated hydrides have been shown to initiate cracks (95). In aluminum and nickel alloys,
Hydrides can form only at much higher hydrogen fugacity than that required for hydrogen embrittlement. The embrittlement mechanism of hydrides is not clearly known. It is thought that the precipitated hydrides behave as other brittle precipitates. They decrease the critical strain for failure by reducing the effective cross section of the specimen when they crack (95).

Westlake (96) was the first who proposed a qualitative mechanism for the stress-induced hydride embrittlement. The basic hypothesis is that the application of tensile stress decreases the hydrogen solute chemical potential at stress concentrators and results in a flux of hydrogen to the region. The hydrogen concentration increases until it attains a value at which time the stress-induced chemical potential gradient is removed. However, the stress also decreases the free energy of the hydride, when it reduces to zero hydride precipitation occurs. In Nb-H system formation of hydrides under stress at stress concentrators and at slip bands has been directly observed using SEM (97,98). It has also been observed that crack propagates through stress-induced hydrides continue to form at the crack tip. Embrittlement in ferrous alloys is less likely to be associated with the formation of the hydride. FeH is stable only in the gas phase.
2.5.4 high pressure bubble formation

High pressure hydrogen filled bubbles have been observed to form in a variety of metals having endothermic heats of hydrogen solution under conditions of high hydrogen fugacity. The bubbles which form can often attain internal pressures of the order of one hundred thousand atmosphere. Propagation of brittle fracture from these high pressure bubbles has been observed (99,100) and appears to serve as a mechanism which reduces the internal pressure.

Hydrogen embrittlement mechanisms based on the formation of high pressure bubble have been proposed (42,101,102). In these mechanisms the driving force for crack growth is the sum of the external stress and the internal pressure. While the internal pressure in the bubble provides an initial driving force for crack propagation, this would decrease rapidly in the absence of a continuous source of high fugacity hydrogen. The observation that fracture often occurs under conditions where such a decrease in bubble pressure must occur as the crack propagates, suggests that the pressurized bubble theory is not sufficient to account for the embrittlement. The support for this conclusion is the observation of
severe hydrogen damage by low pressure hydrogen gas where high pressure bubbles cannot form (103,104).

2.5.5 plastic deformation effects

Stroh (105) originally suggested that hydrogen embrittlement in steels could be accounted for in terms of solution strengthening at the crack tip resulting from dissolved hydrogen with the concomittant decrease in plastic accomodation and blunting and leading to a decrease in fracture toughness. In this model, hydrogen impedes dislocation motion and increases the flow stress. In contrast, Beachem (106) has suggested that stress induced hydrogen segregation at the crack tip aids the plastic deformation processes (slip softening) which lead to failure. It is a view that fracture is an essentially plastic process which is aided by hydrogen. The various failure modes, intergranular, quasi-cleavage or microvoid coalescence, are thought to be the manifestations of the differing microstructures.

Having noted the similarity of intergranular cracking and liquid metal embrittlement in high strength steel, Lynch (107) suggested that surface adsorption can lead to intense localized slip at crack tip, causing crack
propagation by an alternate sliding off the crack tip in a model similar to that suggested by Neumann (108, 109) for fatigue crack propagation. Whether or not such a model occurs should wait until the atomic processes taking place at the crack tip is well understood.

2.6 KINETICS OF HYDROGEN-ASSISTED SUBCRITICAL CRACK GROWTH

2.6.1 The Source of Hydrogen

At all potentials, aqueous sodium chloride solution can supply tremendous amount of hydrated hydrogen ions to the material. When the applied potential is less than the reversible hydrogen potential, hydrated hydrogen ions are reduced at the surface of steel samples. When the applied potential is more noble than the reversible hydrogen potential, hydrogen reduction reaction is inoperative. However, hydrated hydrogen ions can be produced inside the crack tip and pits as a result of anodic dissolution of steel and hydrolysis of oxidized iron. The pH of solution in these partially isolated regions are typically in the range 1-3.5 (46, 110-113); the exact value depends on the solubility product of the hydrolysis reaction and on the particular Pourbaix diagram which applies (46, 114). In this case, hydrated hydrogen ions can also acquire electrons and
form atomic hydrogen at the steel surface. Hydrogen atoms can either combine to form hydrogen molecules and bubble off, can be absorbed into the metal.

2.6.2 Destination of Hydrogen

Regardless the different details of proposed mechanism of hydrogen embrittlement, they all require the accumulation of hydrogen at localized regions for crack initiation. It is, therefore, necessary to know where atomic hydrogen goes once it enters the material. There is a variety of places in a material's microstructure at which the presence of hydrogen may be critical to fracture initiation. These include the lattice itself, other kinds of solutes, grain boundaries, coherent and incoherent precipitates, voids, and dislocations. Segregation of impurities, particularly metaloids, precipitates, such as carbides at grain boundaries and grain boundaries themselves have usually made grain boundaries strong trappings for dissolved hydrogen. For this reason, intergranular crack path has often been observed in cases of high strength steels in hydrogen-containing environments.
On a larger scale, the transport of hydrogen as solute is, however, controlled by the stress distribution. The solution for solute transport in a stressed field has been available for some time now (115, 116). The interaction is given by

\[ U = P \Delta V \]  

(18)

where \( P \) is the pressure tensor of the stress field and \( \Delta V \) is the change in atomic volume due to the insertion of a solute atom. This leads to solution concentration build-up at point within the stress field, given by (116).

\[ C_{eq}^\sigma = C_{eq}^0 \exp \left( \frac{P \Delta V}{kT} \right) \]

(19)

where \( C_{eq}^0 \) and \( C_{eq}^\sigma \) are the equilibrium solute under unstressed and stress fields, respectively. This can be given alternatively as

\[ C_{eq}^\sigma = C_{eq}^0 \exp \left( \frac{\Delta_i V_H}{3R T} \right) \]

(20)
where $V_H$ is the partial molal volume and $\sigma_H / 3$ is the hydrostatic tension. It is apparent that local equilibrium solute concentration is promoted by the hydrostatic tension, and it is maximal in the region of maximum hydrostatic tension, which, as already discussed, lies at a distance of twice of the crack tip opening displacement ahead of the crack tip. Accordingly, hydrogen atoms as solute would migrate by all possible means toward the region of maximum hydrostatic tension to attain thermodynamic equilibrium. This conclusion has been confirmed by extensive studies on high strength steels in both hydrogen atmosphere and electrolytes (117, 118). Isolated intergranular facets have been observed ahead of the crack tip (119, 120).

The most common of transport processes is diffusion through the lattice. Hydrogen diffuses fairly rapidly in metals, particularly in bcc structures such as steels and alpha-Ti alloys. In a non-uniform stress field hydrogen diffusion should follow the Einstein drift equation.
2.6.3 Models of $K_{ISC}$ in hydrogen-containing Environments

In this research, no attempts has been made to understand underlying mechanistic and kinetic basis of the threshold stress intensity, $K_{ISC}$. However, recent advances in the study of kinetic of hydrogen-assisted subcritical crack growth have shown that the crack growth kinetics may well be related to $K_{ISC}$ (115), so a brief review of proposed models for $K_{ISC}$ in hydrogen-containing environments is appropriate.

Gerberich and Chen (115) were the first among researchers suggest that the existence of $K_{ISC}$ for high strength steels in hydrogen-containing environments such as gaseous hydrogen, distilled water, and aqueous sodium chloride, could be established in terms of hydrogen embrittlement mechanisms. The basis of which is that the function of hydrogen is to lower the critical stress for fracture to occur. The basic postulate is that for fracture to occur local equilibrium hydrogen concentration, $C_{eq}$, should be greater than the critical hydrogen concentration at the potential site for fracture. Gerberich and Chen assumed $C_{cr}$ to be constant and $C_{eq}$ to increase
with an decrease in applied stress intensity. $K_{ISCC}$ is, therefore, the stress intensity level at which $C_{cr}$ is equal to $C_{eq}$. It has been shown that elastic consideration of the crack tip fails to predict the existence of $K_{ISCC}$, thereby the plasticity ahead of the crack tip has to be considered (115). Fracture is assumed to occur in the region of maximum hydrostatic tension, where the local equilibrium hydrogen concentration is maximal. The formulation of $K_{ISCC}$ obtained in terms of $C_{cr}$, hydrogen concentration in the elastic bulk, and the yield strength is in qualitative agreement with the experimental observations. Gerberich and Chen also explained in terms of their proposed model the elevation of $K_{ISCC}$ when the stress state varied from plane strain to plane stress.

In the approach of Gerberich and Chen, no micromechanism of fracturing has been assumed, any proposed hydrogen embrittlement mechanism could be used. Implied in their approach, however, the fracture is to initiate on the atomic scale, and the attainment of $C_{cr}$ is a necessary and sufficient condition for fracturing.

Doig and Jones (121) have also established a model for $K_{ISCC}$. There are several similarities between their model and that of Gerberich and Chen. The plasticity ahead of the
crack tip was taken into consideration, and a Ccr was to be achieved for microcrack initiation. However, there is one important difference. Doig and Jones recognized the fact that the critical fracture stresses should be exceeded over a microstructurally significant distance before fracture can occur (122). Accordingly, Ccr = Ceq is a necessary condition rather a sufficient one. Achievement of the fracture stresses over a microstructurally significant distance is another necessary condition. Both conditions should be satisfied in order for fracture to occur.

Doig and Jones have suggested that for mild notches (the crack tip radius is far greater than the microstructural distance) the stress gradient in the region of maximum hydrostatic tension will be low compared with that for sharp cracks. For mild notches, therefore, the peak stresses are likely predominate over a region which is large compared with dc and the controlling parameter becomes simply the critical hydrogen concentration. Implied in the model is that Kiscc increases with the square root of the crack tip radius. The model has also predicted that for $K_i > K_{isc}$, the incubation time decreases with increasing applied stress intensity.
However, Recently, Akhurst and Baker (122) have proposed essentially the same model as that of Doig and Jones. They have successfully explained the independence of Kiscc on hydrogen pressure when it is high. Of the two necessary conditions in the determination of Kiscc, the concentration condition is dominant at high pressure. At fairly high pressures, the critical hydrogen concentration in the region of maximum hydrostatic tension can easily and rapidly be achieved; therefore, the critical stress intensity or stress can be reduced.

2.6.4 **Kinetic Models for Subcritical Crack Growth**

Current kinetic models for subcritical crack growth of high strength steels in hydrogen-containing environments have assumed that the rate-limiting process is the hydrogen migration in the plastic zone around the crack tip by either stress-assisted diffusion (124-127) or dislocation-assisted transport (128).

Proposed models of the first category have essentially the same assumptions of the development of the plastic zone
at the crack tip, limited hydrogen diffusion rate, and, the existence of the critical hydrogen concentration for microcrack initiation. It has generally been assumed in these models that microcrack propagates considerably fast over a finite distance. However, they differ in some other aspects, such as the stress distribution in the plastic zone, the propagation distance of the microcrack, and the relationship between the critical hydrogen concentration and stress intensity.

2.6.4.1 Model Proposed by Van Leeuwen

Besides the above mentioned assumptions, several additional assumptions are involved: (1) the stress in the plastic zone is the plastic zone, (2) micromicrck extend a distance which equal to the minimum width of the plastic zone, and (3) hydrogen diffusion coefficient is constant in both the plastic zone and the elastic bulk (124,125).

The model is essentially to solve the Einstein's drift equation, which takes into account the nonuniform stress field in the sample. Two interesting results obtained from the first approximation of the solution are; (1) for the existence of the Stage II, the critical hydrogen concentration must decrease with increasing stress
intensity, and (2) the existence of KISCC is due to the blunting of the crack tip.

2.6.4.2 Model Proposed by Gerberich, Chen, and St. John

This is the first proposed model which attempted to establish criteria for the existence of stages I, II, and III. There are several differences in the assumptions used between this model and that by Van Leeuwen. Hill's slip-line solution for the stress distribution in the plastic zone given by Wang was employed. The microcracks were assumed to be nucleated over one grain and to extend a grain at a time. Short-time diffusion of hydrogen was assumed, thereby the hydrogen concentration could be ignored, and the hydrogen diffusion was entirely driven by the stress gradient. Further, the hydrogen required to attain the critical value was contributed from the grains in the vicinity of the initiation site of microcrack, which was at the elast-plastic boundary (126).

It was assumed that the difference between the stages I and II was due to the stress state and microstructure of the material. Gerberich et al have observed that the transition from stage I to stage II occurs as the size of the plastic zone at the crack tip is approximately equal to
the grain size. For low yield strength material (tempered at higher temperature), stage I does not exist because of the plastic zone is always greater than the grain size for a given $K_i$ which is greater than $K_{isc}$. Therefore, the stage I crack growth kinetics are predominantly controlled by the elastic stress field, and the stage II crack growth kinetics are predominantly controlled by the plastic stress field. The short-time diffusion correlation of crack growth rate and stress intensity yields, where $d$ is the grain size. For stage III, the crack jump distance is assumed to be the crack-tip opening displacement. The $K_i$ dependence of crack growth rate is It is seen that Equation (a) predicts the stage I crack growth rate linearly dependent on $K_i$. Correlation of Equation (a) and the experimental data is rather poor; the latter shows a much stronger dependence on $K_i$. The dependence of crack growth rate on yield is not explicitly given in Equation (a) and (c). Equation (b) predicts that the stage II crack growth rate is independent of $K_i$ and linearly dependent on yield strength. Gerberich and Chen have noted a difference of two orders of magnitude in stage II crack growth rate with a small change in yield strength (resulting from different tempering temperatures). Such a difference cannot be explained by the changes of yield strength and the critical
hydrogen concentration for microcrack initiation. They suggested that the decrease could be explained in terms of two possible tempering effects on D, that is, tempering could (1) increase the number of effective traps such as precipitates which could give an order of magnitude effect (126). (2) increase the ease of deformation at the crack tip which could produce a difference in void content and dislocation density when loaded. This, in turn, would affect trapping. Equations (a), (b) and (c) predict that the crack growth rate increases with decreasing grain. It is reasonable since the increasing area of grain boundary per unit volume of the material increases the trapping sites of hydrogen atoms. However, it is questionable that at low $K_I$ (in stage I) as the plastic zone is smaller than the grain size, the crack can jump grain by grain.

2.6.4.3 Model Proposed by Raj and Varadan

The model (127) is proposed based on the fact that the crack essentially propagates along the prior austenite grain boundaries. The concept of nucleation and growth used in phase transformation was adopted. It is postulated that the initiation of microcrack requires the formation of a two-dimensional cluster of hydrogen atoms in the grain boundary. As a result of hydrogen diffusion, the cluster
may become large enough to satisfy the Griffith criterion for fracture (surface energy consideration), the microcrack is initiated. The energy barrier is the difference in surface energy between the free surface and the grain boundary.

In addition to the above, a second criterion must be satisfied for the initiation of microcrack. The cluster of H atoms in the grain boundary can become a crack only if the Fe-H-Fe bonds in the cluster can be broken. This requires that the local stress must be above a threshold value which is necessary to break the Fe-H-Fe bonds. This, as suggested by Raj and Vardan, might be the explanation for the existence of Kisc. Accordingly, H atoms have two functions. They are required for weakening the Fe-Fe bondings and the growth of H clusters.

The initiation period of the microcrack was formulated. By assuming no dissociation of the H cluster, the formulated initiation period is an underestimation. The diffusion distance of H atoms to the H cluster was formulated without taking into the consideration of stress. The calculated incubation period is given as follows, where F is a modification factor being equal to 100 and are the surface energies of grain boundary and
fress surface, is the atomic volume of iron, and \( t_{\text{in}} \) is the thickness of grain boundary. Tin was estimated to be on the order of one second. It has been shown that Tin has weak dependence on surface energy, but strongly dependent on the local stress level, which determines the critical size of the H cluster, and, in turn, determines the diffusion distance of H atoms.

It has been suggested that the maximum distance the microcrack could extend is the plastic zone size since once the microcrack reaches the elastic bulk which is relatively more ductile than the plastic region, the crack will blunt. Therefore, the crack growth rate, at high \( K_I \), is linearly dependent on the plastic zone size, and is, in turn, proportional to the square of \( K_I \).

Raj and Vardan was able to explain the strong dependence of crack growth rate on yield strength. They have noted that the local H concentration is exponentially dependent on the local stress level, which is a function of yield strength. In terms of proposed model for \( K_{\text{ISCC}} \), the strong dependence of \( K_{\text{ISCC}} \) on Yield strength could be rationalized in the same way.
2.6.4.4 Model Based on Dislocation Sweeping of Hydrogen

Several recent studies by Chu et al (129) of subcritical crack growth of a high strength steel in hydrogenous environments have raised the speculation rather than lattice or short-circuit diffusion that hydrogen is transported by dislocation sweeping (128). Chu et al followed the subcritical crack growth in conjunction with the observation of crack tip plastic zone development on the surface of WOL specimen. Upon loading, the plastic zone at the crack tip, in the form of two wings as expected for the surface or plane stress state, were observed to grow with time, and the secondary crack initiation occurred when, and at the point where, the growing plastic wings met. Tien et al (130) noticed that the secondary crack did not appear to initiate in the region of maximum hydrostatic tension, which was much closer to the crack tip. Linear elastic fracture mechanics shows that the plane strain plastic zone at the midsection of the section may be wedge-shaped without any elastic enclave at the center and may also be somewhat smaller in size than that at the surface due to plastic constraint. Tien et al, thus, suggested that at the midsection of the specimen, the secondary crack initiated at the elastic-plastic boundary of the hydrogen induced plastic zone and not in the region of maximum
hydrostatic tension either in the air plastic zone or in the time delayed hydrogen induced plastic zone. Furthermore, the distance hydrogen transported by lattice diffusion could not satisfy the experimental observations by Chu et al.

Tien et al propose that cracking can occur at the point where two plastic wings meet since a large excess of H can be made available at this point by a dislocation sweeping mechanism (128). It is imagined that dislocations can move along the plastic wings, dragging a Cottrell atmosphere of H atoms. It is expected that when two plastic wings meet, the annihilation rate of mobile dislocations is very high, leading not only to a large local excess of H concentration at the point of meeting but also, perhaps, to the formation of H filled microvoids followed by a rapid pressurization induced cracking.

Therefore, the model also predicts the discontinuous growth of the primary crack; the rate-limiting process is the development of hydrogen delayed plastic zone. The average subcritical growth rate is then the ratio of the size of hydrogen induced plastic zone to the time taken for the collision of two plastic wings. Since this time is decided by the average sweeping rate in the plastic zone,
thereby, the average subcritical crack growth rate is simply equal to the sweeping rate of mobile dislocation.

However, recently, Tien et al have questioned the existence of the growth of surface plastic zone in hydrogen environments (131). What have been observed by Chu et al appears to be an artifact.

2.7 THE STRESS CORROSION MECHANISM IN HIGH STRENGTH AISI 4340 STEEL IN SODIUM CHLORIDE SOLUTIONS

Studies of the influence of the electrochemical polarization on the cracking of high strength steels in electrolytes have led to the proposal that two types of mechanisms may operate. These mechanisms—active path corrosion (APC) and hydrogen embrittlement—are shown in Figure 21. Figure 21(a) schematically shows APC wherein crack propagation is presumed to occur by anodic dissolution along a preexisting susceptible path in the metal. In this model, Wilde pointed out that the cathodic partial process (hydrogen reaction) serves only as a means of consuming electrons generated by the anodic reaction. Hydrogen embrittlement, Figure 21(b), is principally controlled by production and absorption of atomic hydrogen into the metal at the cathodic sites followed by a hydrogen-induced brittle fracture. The potential or current
Figure 21 Schematic of cracking by active path corrosion (APC) and hydrogen embrittlement (HE) mechanisms.
dependence of the time-to-failure (TTF), may in principle be used to distinguish these phenomena. In Figure 22(b), TTF decreases as cathodic currents are increased with anodic polarization, which has been generally accepted as the evidence of hydrogen embrittlement. The converse is true in Figure 22(c). In which case APC is the proposed cracking mechanism, cathodic protection thereby retarding cracking. Combinations such as Figures 22(a) and (d) were considered to indicate open circuit cracking according to and APC or hydrogen mechanism, respectively. Another test method which has often been used in purpose of verifying hydrogen embrittlement being operative in high strength steel is to compare the time to failure of the specimens tested in aqueous environment under loading modes I and III. As already mentioned, the difference between these two loading modes is that no triaxial stresses exist in the specimen when it is loaded in mode III, then there lacks a driving force to attract hydrogen to the crack tip under loading mode III. Tests conducted on ultrahigh strength maraging martensitic steel stressed in aqueous sodium chloride have shown that the specimen fails in a much shorter time under mode I loading.

However, Truman (45) and later Wilde (44) demonstrated that hydrogen embrittlement was the operative mechanism in
Figure 22 Influence of anodic and cathodic polarization on cracking susceptibility.
both potential regimes. Fractographic evidence which has shown that crack paths in high strength steels at both anodic and cathodic potentials are identical: a primary intergranular following the prior austenite grain boundaries and a secondary (shear) transgranular failure associated with a shear lip (110). The electrochemical basis for the above conclusion is the fact that conditions in localized regions, such as pits and the crack tip, may be quite different from than in bulk electrolyte or on a smooth surface. In particular, Brown et al (46) have shown that the pH measured in the crack tip of 0.45 C steel exposed to aqueous sodium chloride solution was 3.8 regardless of the bulk pH. Hence, even though hydrogen production should not occur at the bulk pH and potential, hydrogen reduction may occur in the crack tip. This conclusion is supported by the studies which show hydrogen permeation through pitted steel polarized to potentials noble to the reversible hydrogen potential (44). Accordingly, the behavior of high strength steel, typified by Figure 22(a), may be interpreted by single mechanism of hydrogen embrittlement at all potentials. At active potentials, hydrogen is produced by the bulk discharge of protons; at noble potentials, the hydrolysis of corrosion products gives rise to local hydrogenation in the crack
tip and pits. In the latter, anodic dissolution is necessary for crack propagation to occur, but it is not the primary embrittling mechanism. While it now seems reasonably well agreed that hydrogen embrittlement is the fracture mechanism of high strength steels at all potentials in aqueous sodium chloride electrolytes, there is without reservation about the basic assumption implicitly used above: hydrogen embrittlement is responsible for the fracture under cathodically polarized conditions. Pickering and coworkers (132-134) have shown that when the cathodic potential is applied to the outer or bulk surface the potential at the crack tip is anodic and anodic dissolution has been observed. Such an observation does not reject the possibility of hydrogen embrittlement as a cracking mechanism; nevertheless, it revives the earlier proposal that both APC and hydrogen embrittlement may be operative and compete with each other in the crack growth process. The influence of anodic dissolution at the crack tip is not exactly known, it may blunt the sharp crack tip or may resharpen a blunted crack tip. Simmons et al (135) have proposed, for steel in distilled water, the following kinetic processes are involved: (1) physical adsorption of water, (2) dissociative chemisorption of water, (3) oxidation of the steel surface and liberation of
hydrogen, (4)) hydrogen entry into the steel, (5) stress-assisted diffusion of hydrogen to the embrittlement sites, (6) the fracture. Auger electron spectra studies of AISI 4340 steel exposed to water vapor showed that the activation energy of the oxidation of iron was comparable to that of crack growth in distilled water. It was, therefore, claimed that the rate limiting step for subcritical crack growth in water was the oxidation of iron and iron carbide. It is, however, to be noted, under controlled electrochemical conditions, the rate limiting step may not be the oxidation of iron and iron carbide since there is sufficient supply of hydrogen ions.

For AISI 4340 steel tested in aqueous solution, the initiation site of the microcrack is not yet exactly known. Although it has been generally accepted that the fracture mechanism of hydrogen embrittlement is the same for the same material whether hydrogen is supplied by internal or external sources, the hydrogen embrittlement kinetics may not necessarily be the same.

A recent study by Page and Gerberich (136) showed that when AISI 4340 steel tested in dilute sulfuric acid (pH = 1.84), the microcrack did not appear to initiate in the region of maximum hydrostatic tension, but at places much
closer to the primary crack tip. It appears that the hydrostatic tension can assist hydrogen diffusion in the plastic zone, but it does not necessarily determine the initiation of the microcrack crack.
Chapter III

EXPERIMENTAL APPARATUS AND PROCEDURES

This chapter is divided into three main sections. The first section describes experimental apparatus. The second section describes the experimental techniques used in this study. The experimental procedures are detailed in the last section.

3.1 EXPERIMENTAL APPARATUS

The experimental setup is shown in Figures 23 and 24. Each part of the setup is described in the following sections.

3.1.1 Material

The high strength AISI 4340 steel, supplied by Republic Steel Co., was prepared by vacuum arc-remelting.
Figure 23 Experimental setup for stress corrosion study.
Table 1
CHEMICAL COMPOSITION OF AISI 4340 STEEL

<table>
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<th>Element</th>
<th>C</th>
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<th>Si</th>
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<td>.28</td>
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</table>
The chemical composition is given in Table 1. The as-received steel plate was 1.59 cm (5/8 inch) thick. The as-received microstructure of the steel is shown in Figure 24. The steel was first cut by flame into pieces of 15.24 cm x 20.32 cm (6 inch x 8 in) prior to final machining. Before being machined, the steel plates were heated at 670°C in an inert atmosphere for 24 hours to reduce the hardness. Following final machining, the steel specimens were given the heat treatment given in Table 2. Also listed in Table 2 are the mechanical properties of the material after heat treatment. Figure 25 shows the resultant microstructure consisting of tempered martensite and...

### 3.1.2 Loading Devices

For static stress corrosion cracking tests, a simple lever-arm system was used to apply load to the specimen. A schematic of the system is shown in Figure 26. The imposition of load on specimen was performed by apply deadweight at the end of the longer arm. The imposed load was measured with a load cell and a strain gauge. The accuracy of loading is 1 kilogram. The variation of applied load was done by a mechanical jack. By adjusting the applied load in accordance with Equation ( ), the required stress intensity could be obtained.
Figure 24 Experimental apparatus for stress corrosion testing.
Table 2

HEAT TREATMENT AND MECHANICAL PROPERTIES
OF AISI 4340 STEEL

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<td>Austenitization</td>
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<tr>
<td>Yield Strength</td>
<td>1547 MPa (224 ksi)</td>
</tr>
</tbody>
</table>
Figure 25 Microstructure of heat-treated AISI 4340 steel.
600X.
Figure 26 Schematic of lever-arm loading system.
Other stress corrosion cracking experiments were performed on Materials Testing Systems testing machine, Figure 27. The "close loop" is a continuous path of interacting elements. If this path is broken at any point while hydraulic pressure is applied to the servovalve, closed loop control is lost and the hydraulic actuator applied full force. Test were conducted in the lowest range necessary in the system to achieve the maximum loads required. All the testings were performed in tension to tension cycling with appropriate waveforms in the load control mode, i.e., the load range was held constant as the crack grew.

3.1.3 Test Cell

All testings were conducted using the corrosion cell shown schematically in Figure (23). The cell was made of Teflon because of its good resistance to 3.5% sodium chloride solution at ambient temperature. Load grips, pull rods, and pins were fabricated from Type 304 stainless steel, which also has good corrosion resistance to the test environment at ambient temperature.
Figure 27 Material Testing System (MTS) testing machine.
3.1.4 Electrochemical Equipment

The control of electrochemical potentials was accomplished with a three-electrode system. A saturated calomel electrode/Luggin probe was used as the reference electrode, Figures 28. The calomel electrode was in a saturated solution of potassium chloride located outside the corrosion cell; it was connected to the test solution by means of a teflon tube with a nylon cord running through it. The cord was saturated with solution to provide conductivity between the two solutions. The Luggin probe salt bridge assembly (Figure 29) was constructed of 3/8 in heavy wall pyrex tubing. A qartz fiber was fused into one end of the probe to provide a slow leak, liquid junction to the saturated calomel reference electrode. The probe tip was not sealed in this fashion to facilitate cleaning after use. The probe was filled with the cell electrolyte through the ground glass joint. Two AISI 304 stainless steel plates were used as counter electrode. During all the testings, they were placed aside and parallel to the specimen to ensure highly uniform current and potential distributions. The potentials were applied by Model 376 two-channel potentiostat manufactured by Princeton Applied Research.
Figure 28 Arrangement of counter and reference electrodes, and specimen, for potentiostatically controlled experiments.
Figure 29 Luggin probe.
3.1.5 Measurement Devices

Crack length were measured in two ways. Before and after all the testing, the crack length was measured optically on the specimen surface with a Gaertner 50x travelling microscope. The crack length could be determined to 0.005 in. During the testing, crack lengths were measured via the compliance technique using a linear variable differential transformer (LVDT).

The LVDT is an electromechanical transducer that produces an electrical voltage output proportional to the displacement of a separate movable core. When the core is in the center position, the voltage output is zero; when the core is moved, a differential voltage is induced, which varies linearly with changes in the core position. The calibration of the Shaevitz LVDT is given in Figure 30. The conversion factor for voltage output of LVDT and the core movement is 100.52 volts/inch.

The LVDT was mounted to the specimen with teflon blocks and extension tubes are shown in Figure 23. The LVDT body was mounted to one side of the machined notch, while the core was attached to the other side. Thus, as
Figure 30 Calibration of linear variable differential transducer.
the crack extended, the crack opening made the core of LVDT move and produced a voltage difference.

3.2 EXPERIMENTAL TECHNIQUES

3.2.1 Specimen Design

In order to control the stress intensity level at the crack tip, $K$, contoured double cantilever beam (contoured DCB) specimens as shown in Figure 31 were used. A properly designed contoured DCB specimen can produce a stress intensity level that is independent of crack length over several centimeters.

In this study, contoured DCB specimens were designed on the basis of calibration data provided by Smith et al, Table 3 (12). The geometrical parameters are given as follows: $H/e = 0.3$, $W/e = 4.8$, $W = 18.1$ cm ($7\,1/8$ inch), and $B = 1.27$ cm ($1/2$ inch), Figure 32. The geometrical parameters yield a stress intensity for a smooth specimen of

$$K = 3.654 \times 10^{-2} \text{ (MPa$\sqrt{m}$)}$$ (21)
Figure 31 Geometry of contoured DCB specimen.
### Table 3 Design data for constant Ki specimen.

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\(KBW^{1/2}/p\)

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Figure 32 Values of geometric parameters for contoured DCB specimen used in this study.
for $a/W = 0.2$ to $0.5$. The dimensions of $K$ and $P$ are $\text{MPa}\sqrt{\text{m}}$ and $K_g$, respectively. Side grooves were introduced along the crack plane of the specimen to enhance plane strain and to guide the direction of crack. The relationship between $K$ and $P$ for the side-grooved specimens was determined experimentally by using the compliance measurement, since no literature data were available for this case. The result of compliance measurements for several crack length are given in Figure 33. It is seen that the compliance is essentially linearly dependent on crack length. Therefore, the compliance can be expressed as follows:

$$C = \lambda a + \eta$$  \hspace{1cm} (22)

with $\lambda = 2.191 \times 10^{-8}$ gm and $\eta = -3.494 \times 10^{-8}$ cm/gm for $a = 3.4$ to 9.5 cm. Mode I stress intensity, defined in terms of the compliance, is given by

$$K_I = EP^2/2B \left( \frac{dC}{da} \right)$$  \hspace{1cm} (23)
Figure 33 Compliance versus crack length data for the contoured DCB specimen shown in Figure 32.
where $E$ is Young's modulus, $2.07 \times 10^8$ MPa. Combination of Equations (22) and (23) yields

$$K_I = 4.972 \times 10^{-2} P \sqrt{\text{m}} \quad (24')$$

It is obvious that side-grooved specimens endure higher stress intensities than do smooth specimens under equal loads. The elevation of stress intensity due to the presence of side grooves conventionally has been expressed in the form (18):

$$K'_I = (B/B_N)^m K_I \quad (25)$$

where $K_I$ and $K'_I$ are the stress intensities of smooth and side-grooved specimens under equal loads, and $B$ and $B_N$ are the full and side-grooved thicknesses. The parameter $m$ is a constant, which, in theory, should be equal to 0.5.

In practice, a reasonable value for $m$ is between 0.5 and 1 (18). Combination of Equations (21) and (24), and using the values of $B$ and $B_N$, yields $m = 0.585$. The deviation of $m$ from the theoretical value 0.5 is believed to be the result of the removal of a finite amount of material due to side-grooving.
One side-grooved specimen was employed to determine the fracture toughness of the material, $K_{IC}$. Load on the specimen was started with a low value and then increased in steps of 2 kilograms. The critical load on the specimen was then found as the crack started to extend unstably. The critical stress intensity, $K_{IX}$, is equal to $K_{IC}$ if the geometry of the specimen satisfies the plane strain conditions, i.e.,

$$B > 2.5 \left( \frac{K_{IX}}{N} \right)^2$$

(26)

where $\sigma_y$ is the yield strength of the material, and $a_0$ is the length of the machined notch. Substituting the values of $K_{IX}$ and Equation (26) yields that the minimum linear dimension of the specimen satisfying plane strain conditions should be 0.32 cm (0.124 inch), which was much less than $B_N$ and $a_0$. Therefore, plane strain conditions were satisfied by the specimen, and hence $K_{IX} = K_{IC}$. Fracture toughness, $K_{IC}$, of the material was found to be 67.2 MPa$\sqrt{m}$. 
3.2.2 Specimen Preparation

Each specimen was sanded to fine finish with SiC 600 grit sand paper to provide a uniform surface finish. All the sandings was done in a direction parallel to the crack propagation. The specimens were coated with silicone rubber sealant to prevent general corrosion of all but the side-grooved regions, since corrosion could affect the compliance of the specimens. The most susceptible areas, for example the necks of specimens, were also protected with adhesive tape. Before all the tests, specimens were rinsed in acetone. The specimens were coated with silicone rubber sealant to prevent general corrosion of all but the side-grooved regions, since corrosion could affect the compliance of specimens. The most susceptible areas, for example, the necks of specimens, were also protected with adhesive tape. Load grips, pins and the portion of loading bars exposed to the test environment were also coated with silicone rubber sealant. Therefore, galvanic corrosion would not occur and the electrochemistry of the system would not be affected.
3.2.3 **Precracking Procedures**

All the specimens were fatigue precracked in air to an average of 0.06 inches beyond the machine notch. There were two purposes of precracking. The first was to generate a crack in the specimen with a stress intensity history which was known. The second was to produce a sharp crack tip with a small plastic zone size sufficiently distant from the machined notch so as to be free from residual stresses resulting from machining.

Fatigue precracking was completed in the load control, tension to tension sinusoidal mode by the use of MTS testing machine. The precracking procedure was accomplished in a series of steps starting with higher maximum stress intensity, $25 \text{ MPa/V}$, and decreasing to a lower maximum stress intensity. In the last step, the maximum stress intensity used was $9 \text{ MPa/V}$. The minimum stress intensity used was $4 \text{ MPa/V}$. The initial use of higher maximum stress intensity was purported to create a fatigue crack in a short period of time. However, higher maximum stress intensity would give larger plastic zone and which is undesirable for the testings. The lower maximum stress intensities, which was used later, was to ensure to the sharpness of fatigue cracks. All fatigue precrackings were done at a frequency of 10 Hz.
3.2.4 Crack Length Measurement

The simple and straightforward method for crack length measurement is by visually determining the distance between the loading line and the crack tip along the crack plane at the specimen surface. Because the stress distribution at the crack tip varies from the surface toward the center of the specimen, the crack front resulting from subcritical crack growth, such as stress corrosion, hydrogen embrittlement, and fatigue, is usually curved. The curvature of the crack front is also controlled by the thickness of specimen, chemistry of environment, and microstructure of the material. Consequently, the crack length used is to be the average value over the specimen thickness. In general, for smooth specimens, where plane stress predominates at the surface, the crack front is usually convex toward the cracking direction. Therefore, surface measurement underestimates the crack length. On the contrary, for side-grooved specimens, the crack front is usually concave toward the crack direction, an over-estimate of the crack length is given by the surface measurement.
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In order to know the curvature of the crack front and determine the average crack length, one should break the specimen. However, it is impractical in most cases when continuous monitoring of the crack length is required. An approximation method was used in this research. One specimen was broken in air after stress corrosion testing at \( K = 26.4 \text{ MPa}\sqrt{\text{m}} \) (this value was later calculated from the exact compliance calibration). Based on the obtained curvature of the crack front, a correlation between the average crack length and that obtained by surface measurement was established. By assuming the same curvature of the crack front at other stress intensity levels, the average crack length can be determined by visual observation at the specimen surface. In practice, the visual determination of the crack length was done by loading the specimen by a MTS testing machine. By opening the crack, the crack tip could be easily located and the crack length was accurately measured with a travelling microscope. The modified visual method was applied to the calibration of the compliance of the contoured DCE specimen. It was also employed to determine the crack length before and after each test. No visual determination of the crack length was made during the tests because the crack tip was usually obscured by the corrosion products.
and/or by the counter electrodes. However, after termination of an experiment, the corrosion products were removed from the side grooves with 600 grit SiC paper and the crack length was measured using a 50x travelling microscope. In general, excellent agreement was found between the indirect and direct crack length measurements.

The indirect method employed for crack length measurement was the compliance method. It is clear shown in Equation (22) that the compliance of the specimen is a function of crack length. Under constant $K$ conditions, applied loads are constant, so that the crack length can be determined by the measurement of the crack opening displacement along the load line, $\delta$.

A linear variable differential transducer (LVDT) was used to measure $\delta$. The LVDT has been designed in such a way that a change in $\delta$ is linearly proportional to the accompanying change in the voltage output of LVDT. For the ease of alignment and possible disturbance of the system by the presence of LVDT, instead of being placed along the load line. The LVDT was attached to the edge of the specimen and centrally located in respect to the specimen thickness. Therefore, it was the crack opening displacement
along the edge, $\delta_g$, being measured. $\delta$ and $\delta_g$ can be correlated by the principle of similar triangles, Figure 34.

$$\delta = \frac{a}{a+d} \delta_g \quad (27)$$

where $d$ is the distance between the load line and the gage line, and is equal to 3.81 cm (1.5 inch). Combination of Equations (22) and (27) yields

$$a = \frac{1}{A_1} (\sqrt{A_2^2 - A_1 A_3} - A_2) \quad (28)$$

where

$$A_1 = P\lambda$$
$$A_2 = (P\eta + Pd\lambda - \delta_g)/2$$
$$A_3 = Pd\eta$$

Equation (28) was employed to determine the initial and final crack lengths. In general, crack lengths measured by the direct and indirect methods are in excellent agreement.
Figure 34 Correlation of load line and gage line crack opening displacements.
3.2.5 Crack Length Determination

The method employed for the calculation of instantaneous crack length during the testing is described below. Let \( L(0) \) be the initial voltage output of LVDT at the start of the test, \( a(0) \) be the initial crack length, and \( P \) be the applied load. \( \delta g(0) \) can be calculated by substituting values of \( a(0) \) and \( P \). Also, \( \delta g(0) \) is related to the outputs of LVDT by

\[
\delta g(0) = b (L(0) - L_x) \tag{29}
\]

or

\[
L_x = L(0) - \frac{\delta g}{b} \tag{30}
\]

where \( b \) is the proportionality constant, and \( L_x \) is the output of LVDT when no load is applied to the specimen. Therefore, at a certain time, the crack opening displacement along the gage line is

\[
\delta g(t) = b (L(t) - L_x) \tag{31}
\]
Combination of Equations (22), (23), (27) and (31) yields

\[ a(t) = \left( \frac{1}{A_1} \right) \left( \sqrt{A_4^2 - A_1 A_3 - A_4} \right) \]

(32)

where

\[ A_4 = \left( \frac{P_f + -A_B}{2} \right) \]

\[ A_5 = b(L(t) - L(0)) + \frac{\delta}{g(0)} \]

3.2.6 Crack Growth Rate Determination

An incremental polynomial technique was used to calculate crack growth rate. This method involves fitting a second order polynomial to sets of seven consecutive crack length vs. time data points. The least square method was used to determine the polynomial which produces minimal overall deviation. The crack growth rate at the center point was then obtained by differentiating the polynomial and substituting in the appropriate value of time. For the first and last there data points, the second order approximations for the first and last seven data points were used respectively.
Crack growth rates were presented graphically as a function of time for a particular load (stress intensity) history. The steady-state crack growth rates were also presented in the conventional crack growth rate (on logarithm scale) and stress intensity correlation.

3.3 EXPERIMENTAL PROCEDURES

Loading histories of experiments conducted in this study were divided into the following categories:

1. Loading Scheme I: Sudden increase of stress intensity at stationary cracks.
2. Loading Scheme II: Sudden increase of stress intensity at growing cracks.
3. Loading Scheme III: Sudden decrease of stress intensity at growing cracks.
4. Loading Scheme IV: Decrease of stress intensity at growing cracks at finite rates.
5. Dynamic stress corrosion cracking.
3.3.1 **Test Environments**

The electrolyte used was 3.5% NaCl aqueous solution, which was made of reagent grade salt and double distilled, demieralized water. Ph values of the electrolyte were in the range of 6.8-7.2. There were two reasons why sodium chloride solution was used instead of using distilled water. Firstly, according to the available test data, the stress corrosion cracking behaviors in AISI 4340 steel in distilled water and in 3.5% NaCl solution are essentially the same. Secondly, the sodium chloride solution has much higher electrical conductivity than distilled water, so electrochemical control can be easily completed without the hindrance of IR drop. The tests were conducted at ambient temperature, which was typically 25°C. All the testing was conducted under well-defined electrochemical conditions. The potentials employed in this study include one cathodic (-1.0 V\text{SCE}), the open-circuit (-0.61 V\text{SCE}), and an anodic (-0.55 V\text{SCE}) values.

3.3.2 **Loading Schemes**
3.3.2.1 Loading Scheme I

Specimens were initially loaded at \( K = 9 \text{ MPa}\sqrt{\text{m}} \). The loads were then raised in step fashion to give the stress intensities, which presumably within the Stage II regime of the crack growth rate vs. stress intensity correlation. The upper stress intensities employed were 20, 30, and 35 MPa\sqrt{\text{m}} (Figure 35). For a given increased, three different controlled electrochemical potentials were employed. They were a cathodic \((-1.0 \text{ V}_{\text{SCE}})\), open-circuit \((-0.61 \text{ V}_{\text{SCE}})\), and an anodic \((-0.55 \text{ V}_{\text{SCE}})\). The crack propagation responses were recorded.

3.3.2.2 Loading Scheme II

The tests were designed to study the crack growth response to sudden increases in the applied stress intensity at growing cracks. The specimen which was initially loaded at \( K = 9 \text{ MPa}\sqrt{\text{m}} \) was loaded to 20 MPa\sqrt{\text{m}}. The increase in the applied stress intensity was made after the crack propagated at the steady-state rate characteristic of \( K = 20 \text{ MPa}\sqrt{\text{m}} \). The final stress intensities employed were 25, 30 and 35 MPa\sqrt{\text{m}}. The loading history is shown schematically in Figure 36. The testings were conducted under controlled potentials which were stated above.
Figure 36 Loading Schemes II and III.
3.3.2.3 Loading Scheme III

The test procedure used were essentially the same as the previous subsection. The initial stress intensity employed was 35 MPa/\(\sqrt{m}\). However, in this loading scheme, the stress intensity at a growing crack was suddenly reduced, Figure 36. The final stress intensities employed were 20, 25 and 30 MPa/\(\sqrt{m}\).

3.3.2.4 Loading Scheme IV

The testing procedures were essentially the same as those employed in the previous subsection. The only difference is that now the decrease of the applied stress intensity was kept at a finite rate (Figure 37). \(T\) is the time period taken for the completion of the decrease of the applied stress intensity. It was the purpose of the tests to know how the crack growth responded to the changing rate of the stress intensity. The crack growth responses after the completion of the change in the stress intensity were recorded. For a given decrease in the applied stress intensity, the tests were started with a low value of \(T\).
Figure 37 Loading Scheme IV.
The values of $T$ were gradually increased for the next tests until no incubation and transient periods were observed.

### 3.3.2.5 Dynamic Stress Corrosion Cracking

All the previous tests were aimed at realizing the crack growth responses under single perturbations. The present testings were aimed at studying how the crack growth responds to repeated perturbations. Also, it was attempted to know whether these different studies could be correlated and rationalized in terms of a unified mechanism.

The wave forms employed were square, positive sawtooth, and negative sawtooth wave forms, Figure 38. In practice, these wave forms are extreme cases and rarely encountered. Each of these wave forms represents a simple and special case. For square wave forms, the change between maximum and minimum stress intensities is made at extremely fast rate; and there is holding at either maximum or minimum stress intensity level. On the contrary, no hold at maximum and minimum stress intensities exist for sawtooth wave form. Positive and negative wave forms are diametrically opposite. For positive sawtooth wave forms,
Figure 38 Waveforms employed for dynamic stress corrosion cracking. (a) square, (b) positive sawtooth, (c) negative sawtooth.
the increasing rate of the apparent stress intensity is much smaller than the decreasing rate of the apparent stress intensity in a cycle. Whereas for negative sawtooth wave forms, the decreasing rate of the apparent stress intensity is much smaller than the increasing rate of the apparent stress intensity in a cycle. The stress intensity perturbation employed were 4 and 10 MPa√m. All the testings were conducted under the potentiostatically controlled open-circuit potential.
Chapter IV
EXPERIMENTAL RESULTS

4.1 POLARIZATION CURVE

The polarization curve of AISI 4340 steel in aerated 3.5% NaCl aqueous solution is shown in Figure 39. It is clearly shown that no passive region exists above the open-circuit potential (\(-0.61\text{V}_{\text{SCE}}\)), which frequently observed for many engineering alloys. The current increases dramatically with the small increment of potential above the open-circuit potential. When the potential was made more negative away from the open-circuit potential, the increasing rate of current is gradually decreased, and it finally is saturated. From the fundamental electrochemistry, it is understood that it is hydrogen revolution redominates when the potential is more negative than the open-circuit potential. On the other hand, the oxidation of the alloy predominates as the potential is more positive than the open-circuit potential.
Figure 39 The polarization curve of AISI 4340 steel in aerated 3.5% NaCl solution, at room temperature.
4.2 RESULTS OF LOADING SCHEME I

Figure 40 is a typical LVDT output recorded by strip chart recorder showing the variation of the crack length after a sudden application of stress intensity. The experimental results given in Figures 41-43 show that, upon sudden application of a certain stress intensity above Kiscc, the crack grew only after an incubation period. At any given potential, the incubation period was decreased with increasing applied stress intensity. At a given stress intensity level, the incubation period was increased as the applied potential became more positive. Furthermore, once the crack started to propagate, it did not extend at a constant rate, even though the applied stress intensity was maintained constant. Instead, the crack growth rate increased monotonically with time towards a constant steady-state value which depends on the applied stress intensity and applied potential. The existence of the incubation and transient periods, as found, is consistent with the results by Wei and Landes (26,27).

The dependence of the steady-state crack growth rate on applied stress intensity and potential are shown in Figure 44. Two significant points may be gleaned from these
Figure 40 LVDT output shows a typical crack length response to a sudden application of a stress intensity greater than $K_{ISCC}$. 
Figure 41 Crack growth responses to Loading Scheme I at $E = -1.00 \text{V}_{\text{SCE}}$. 

Potential $E = -1.0 \text{V}_{\text{SCE}}$ 

- $K_{II} = 9 \text{MPa}\sqrt{\text{m}}$
- $K_{II} = 35 \text{MPa}\sqrt{\text{m}}$
- $K_{II} = 30 \text{MPa}\sqrt{\text{m}}$
- $K_{II} = 20 \text{MPa}\sqrt{\text{m}}$

Crack Growth Rate $\times 10^3 \text{cm/min}$ vs. Time, min
Figure 42 Crack growth responses to Loading Scheme I at $E = -0.61 V_{SCE}$. 

Potential $E = -0.61 V_{SCE}$

$K_{II} = 9 MPa\sqrt{m}$

$K_{II}$

Crack Growth Rate x10³ cm/min

- $K_{II} = 35 MPa\sqrt{m}$
- $K_{II} = 30 MPa\sqrt{m}$
- $K_{II} = 20 MPa\sqrt{m}$

Time, min

Figure 42 Crack growth responses to Loading Scheme I at $E = -0.61 V_{SCE}$. 

Potential $E = -0.61 V_{SCE}$

$K_{II} = 9 MPa\sqrt{m}$

$K_{II}$

Crack Growth Rate x10³ cm/min

- $K_{II} = 35 MPa\sqrt{m}$
- $K_{II} = 30 MPa\sqrt{m}$
- $K_{II} = 20 MPa\sqrt{m}$

Time, min
Figure 43 Crack growth responses to Loading Scheme I at \( E = -0.55\,V_{SCE} \).
Figure 44 Dependence of the steady-state crack growth rate resulting from Loading scheme I on stress intensity and potential.
data. Firstly, at a given electrochemical potential, the steady-state crack growth rate increases with stress intensity. Since the variation of the steady-state crack growth rate is relatively small (less than an order of magnitude), it is apparent that the applied stress intensity lies within the Stage II region of the crack growth rate (on a log scale) versus stress intensity correlation obtained by using DCB or WOL specimens. Secondly, at a given stress intensity level, the steady-state crack growth rate increases as the applied electrochemical potential is made more negative. The transient period, namely, the time taken for a crack to grow at a steady-state crack once it starts to propagate, does not exhibit a simple dependence on applied stress intensity at a given electrochemical potential. However, at a given stress intensity level, the transient period was found to decrease as the potential was made more negative. The total time taken for the crack to achieve a steady-state growth rate from the moment the stress intensity was changed, (i.e. the sum of the incubation and transient times) increases with decreasing applied stress intensity at a given potential; whereas at a given stress intensity level, it increased at the applied potential was made more positive (Figure 45). The stress corrosion crack path is
Figure 45 Dependence of incubation period + transient period on stress intensity and potential.
intergranular; it follows the prior austenitic grain boundaries, Figure 46(a). The difference between the fracture mode is shown in Figure 46(b). The stress corrosion fracture surface is on the left-hand side. On the right-hand side, it is the fracture pattern of a fast fracture in air when the specimen was loaded to Kic of the alloy. Dimples can be clearly seen; the fracture is ductile in nature.

4.3 RESULTS OF LOADING SCHEME II

Essentially no incubation and transient periods were observed upon sudden increase of the apparent stress intensity at a growing crack at the open-circuit or cathodic potentials; the crack immediately propagated at a steady-state rate characteristic of the final stress intensity. When the system was anodically controlled, upon sudden increasing the applied stress intensity at a growing crack, incubation and transient periods were observed, in contrast to the behaviors under the open-circuit and cathodic potential conditions. In this case, the incubation and transient periods do not exhibit a clear dependence on the amount of the stress intensity increased (Figures 47-49). A comparison of experimental results
Figure 46 Fractographies of AISI 4340 steel resulting NaCl at $K_i = 30$ MPa m, $E = -0.61V$, and (b) fast fracture in air.
Figure 47 Crack growth responses to Loading Scheme II

$k_{ii} = 20 \text{ MPa} \sqrt{\text{m}}$, $E = -0.55 V_{SCE}$
Figure 48 Crack growth response to Loading Scheme II, $K_{II} = 25$ MPa $\sqrt{\text{m}}$, $E = -0.55 V_{SCE}$. 

$E = -0.55 V_{SCE}$

Crack Growth Rate $\times 10^3$ cm/min

Time, min.

$K_{II} = 25$ MPa $\sqrt{\text{m}}$

$K_{II} = 35$ MPa $\sqrt{\text{m}}$
Figure 49 Crack growth response to Loading Scheme II, 
$K_{II} = 30 \text{ MPa} \sqrt{\text{m}}$, $E = -0.55V_{SCE}$
obtained from Loading Schemes I and II exhibits that the steady-state crack growth rates at are essentially the same. It implies, that, the steady-state crack growth rate depends on the final stress intensity and is independent of the loading history despite that the overall crack growth responses being dependent on loading history.

4.4 RESULTS OF LOADING SCHEME III

A typical crack growth response is shown schematically in Figure 50. The crack growth responses to the sudden decrease of applied stress intensity at a growing crack are shown in Figures 51-53. Upon suddenly decreasing the applied stress intensity at the tip of a growing crack, the crack immediately stopped growing. The crack started to grow only after an incubation period. The crack did not propagate at a steady-state rate, even the apparent stress intensity was maintained constant, until a transient period elapsed. The duration of the incubation and transient periods was found to increase with increasing reduction in applied stress intensity (Figure 54). This observation is in qualitative with the results the observations of Dull et al. (30), and of Aoki et al. (119). Further, for a given reduction in the applied stress intensity, the
Figure 50 Schematic of the variation of the crack length under Loading Scheme III. Stress intensity is decreased at $T^*$. 
Figure 51 Crack growth responses to Loading Scheme III at $E = -1.00V_{SCE}$. 

$K_{II} = 35 \text{MPa} \sqrt{\text{m}}$

- $K_{II} = 30 \text{MPa} \sqrt{\text{m}}$
- $K_{II} = 25 \text{MPa} \sqrt{\text{m}}$
- $K_{II} = 20 \text{MPa} \sqrt{\text{m}}$
Figure 52 Crack growth responses to Loading Scheme III at $E = -0.61V_{SCE}$. 

- $K_{II} = 35 \text{ MPa} \sqrt{\text{m}}$
- $K_{IF} = 30 \text{ MPa} \sqrt{\text{m}}$
- $K_{IF} = 25 \text{ MPa} \sqrt{\text{m}}$
- $K_{IF} = 20 \text{ MPa} \sqrt{\text{m}}$
Figure 53 Crack growth responses to Loading Scheme III at $E = -0.55V_{SCE}$. 
Figure 54 Dependence of incubation period + transient period on stress intensity history and potential under Loading Scheme III.
duration of the incubation and transient periods appeared to increase as the electrochemical potential was made more positive. The steady-state crack growth rates were again found to be independent of the stress intensity history.

It is clear from the crack growth responses obtained from the sudden increase and decrease of the applied stress intensity at growing cracks that the crack propagation would momentarily stop and regain a steady-state crack growth rate after an incubation period of no crack propagation and a transient period of monotonically increasing crack growth rate. However, the duration of the incubation and transient periods is a strong function of the stress intensity history. It is relatively short if the stress intensity is increased. On the contrary, it is relatively long when the applied stress intensity is decreased.

4.5 RESULTS OF LOADING SCHEME IV

It was confirmed by previous experimental results that a sudden decrease of the applied stress intensity at a growing crack resulted in the halt of the crack propagation. Figures 55-57 show the effect of decreasing
Figure 55 Crack growth response to Loading Scheme IV, $K_{if} = 20 \text{ MPa}\sqrt{\text{m}}$.
Figure 56 Crack growth response to Loading Scheme IV, $K_{IF'} = 25$ MPa/√m.
Figure 57 Crack growth response to Loading Scheme IV, $K/I_f = 30\,\text{MPa}\sqrt{\text{m}}$. 
rate of the applied stress intensity on the crack growth behavior. The applied stress intensity was increased. There were two variables involved in this set of experiment. They were the amount of the reduction in the applied stress intensity and the time taken for the completion of the reduction of the applied stress intensity, T. The effects resulted from singly varying each of these variables are summarized below:

The effects of T:

1. The duration of the incubation and transient periods was decreased as T was increased.
2. No incubation and transient periods existed as T was made greater than a certain value, Tcr.

The effect of the reduction in the applied stress intensity:

1. The duration of the incubation and transient periods was increased as the change in stress intensity was increased.
2. Tcr was increased as the change in stress intensity was increased.

Imagine that if the decreasing rate of the applied stress intensity is extremely small, the crack growth rate may well follow the instantaneous applied stress intensity;
therefore, the experimental results obtained are reasonable.

4.6 RESULTS OF DYNAMIC STRESS CORROSION CRACKING

Because of the special purpose of this study, the crack growth rates resulted from dynamic study are expressed on time base and compared with that obtained under sustained loading at the mean stress intensity ($K_{im} = 30$ MPa m), instead of being expressed as the increment of crack length per cycle as often being done in corrosion fatigue studies. The experimental results are shown in Figures 58-59. There were three parameters in this set of testing, namely, frequency, stress intensity amplitude, and waveforms. The effects of these parameters are summarized below:

1. Dynamic stress corrosion crack growth rates are lower than that obtained under sustained loading at the mean stress intensity.

2. For a given stress intensity amplitude and waveform, the crack growth rate decreases with increasing frequency.
Figure 5b Dynamic stress corrosion crack growth rates,
\[ K_{\text{Im}} = 30 \text{ MPa}\sqrt{\text{m}}, \Delta K_{\text{l}} = 4 \text{ MPa}\sqrt{\text{m}}. \]
Figure 59 Dynamic stress corrosion crack growth rates, $K_{m} = 30 \text{ MPa}\sqrt{m}$, $\Delta K = 10 \text{ MPa}\sqrt{m}$. 
3. For a given frequency and waveform, the crack growth rate decreases with increasing stress intensity amplitude.

4. For a given frequency and stress intensity amplitude, the crack growth rate is highest under square wave form; it is lowest under positive sawtooth waveform.
Chapter V
DISCUSSION

It is generally accepted that subcritical crack growth in high strength AISI 4340 steel in 3.5% sodium chloride solution at ambient temperature is a consequence of hydrogen embrittlement (44-46). Such a mechanism is supported by experimental results of this study. The steady-state crack growth rate, at a given stress intensity, increases as the applied electrochemical potential is made more negative. Also, the crack growth response to Loading Schemes I, II, III, and IV exhibit a consistent trend that the incubation and transient period becomes shorter when the applied electrochemical potential is made more negative. Further, it is shown in the polarization curve of the system that no passive region exists. Therefore, it appears that no film is involved in the fracture process.

In terms of hydrogen embrittlement mechanism, the subcritical crack growth kinetics can be considered to
include several consecutive processes. Consider the processes occurring at a pre-existing crack under controlled electrochemical potential. Hydrogen ions are, first, reduced to atomic hydrogen at the alloy surface. Some of atomic hydrogen can combine to form gaseous hydrogen and, then, bubble off. Others can be absorbed on the surface. Because of the great hydrogen concentration difference existing between the surface and the lattice, absorbed hydrogen atoms will migrate into the alloy by volume diffusion and/or short-circuit diffusion along grain boundaries. Hydrogen atoms, then, accumulate at certain places and initiate microcrack by a certain hydrogen embrittlement mechanism. When the microcrack forms it immediately propagates.

The exact effect of stress intensity on hydrogen adsorption at the crack tip is not known. It was assumed by Cherepanov (137) that hydrogen adsorption increases with applied stress. It appears reasonable that when the applied stress intensity increased, crack tip area exposed to the environment is increased. As a result, hydrogen adsorption can be enhanced. Or, the dissolution in the vicinity of the crack tip can be increased. As a result, under controlled electrochemical potential, hydrogen reduction and, in turn, hydrogen adsorption at the crack tip is increased
accordingly. However, it is noticed that under cyclic loading condition, the possibility of crack-tip closure should not be ignored. When the applied stress intensity is less than the crack-tip closure stress intensity, the crack tip is closed and isolated from the environment, the hydrogen adsorption does not increase with applied stress intensity.

When a cracked alloy is stressed, a plastic zone is formed at the crack tip. It is not exactly known the effect of plasticity at the crack tip on hydrogen diffusivity in high strength steels. Reported data of hydrogen diffusivity in a unstressed steel has several orders-of-magnitude difference depending on the methods employed to measure it. It has been found that hydrogen diffusivity is increased when the steel is elastically stressed. However, no data of hydrogen diffusivity in a plastically deformed region is available. It is believed that the plasticity can affect the hydrogen diffusivity, but its effect is not significant compared with uncertainty of hydrogen diffusivity data in a unstressed steel. Therefore, hydrogen diffusivity is assumed to be invariant with the stress state.
The diffusion of hydrogen atoms is not only driven by the concentration difference, it is also driven by hydrostatic tension existing in a stressed component. Hydrogen atoms will diffuse in accordance with Einstein equation to achieve equilibrium concentration in commensurate with local stresses. Hydrogen atoms has great tendency migrating toward the regions of maximum hydrostatic tension, which lies about twice of the crack tip opening displacement ahead of the crack tip, according to the calculation by Rice and Johnson for the condition of small scale yielding. Therefore, hydrogen flux is higher in the vicinity of the crack tip; and it can be expected that the microcrack initiates in the vicinity of the tip of the pre-existing crack.

Studies of fast fracture in a brittle mode indicates that for fracture to occur, the critical fracture stress must be exceeded over a microstructurally significant distance (120). Since the subcritical crack path in high strength AISI 4340 steel in 3.5% sodium chloride solution is predominately brittle along prior austenitic grain boundaries. It is reasonable to assume that the same requirement should be satisfied for fracture to occur. The effect of hydrogen is mainly to reduce the critical fracture stress.
When the fracture requirement is satisfied, a microcrack is initiated and rapidly propagates under the control of tensile stress normal to the crack plane. The microcrack initiation site is determined by hydrogen distribution ahead of the crack tip, which is, in turn, determined by hydrogen flux. It is noted that in aqueous solution, there is only external hydrogen source. Although the maximum stresses is at some distance away from the crack tip, the microcrack does not necessarily initiate in the regions of maximum hydrostatic tension because hydrogen concentration is maximum at the crack tip. Therefore, it is suggested, here, that the microcrack initiation site is right in the region at the crack tip. The microcrack rapidly propagates away from the initiation site if the local stress is sufficient. It then may arrest if it encounter a barrier; an intergranular crack may branch at a grain boundary junction. It may even arrest simply because it is propagating into a region of rapidly decreasing stress and/or hydrogen concentration. Hydrogen diffusion is again required for the next event of the microcrack initiation and propagation.
5.1 STATIONARY CRACKS

5.1.1 Incubation period

The existence of the incubation period is, therefore, a consequence of the delay due to hydrogen diffusion towards and accumulation at hydrogen traps in achieving the critical hydrogen concentration and the critical nucleus size. Because the flux of hydrogen atoms, and hence the time taken to achieve the critical conditions for the microcrack initiation, is affected by both applied stress intensity and applied electrochemical potential; the incubation period also depends on these two intensive variables. Since hydrogen adsorption at the crack tip region presumably increases with applied stress intensity; therefore, for a given electrochemical potential, the higher the applied stress intensity, the higher the accumulation rate of hydrogen atoms at traps. It can be expected that the incubation period is decreased when the applied stress intensity is increased. The difference in the incubation period decreases as the applied stress intensity is increased. The reason appears to be that the region of maximum hydrostatic tension is gradually shifted away from the crack tip as the applied stress intensity is
increased, while the maximum hydrostatic tension maintains unchanged.

At a given stress intensity, the effect of electrochemical potential is the enhancement of the surface absorption of hydrogen atoms, and, therefore, the ingress rate of hydrogen atoms into the lattice. Hence, the incubation period, at a given stress intensity, is decreased as the applied electrochemical potential is made more negative.

5.1.2 Transient period

The primary crack extends a finite distance once the microcrack is initiated and immediately ruptures. Once the crack starts to propagate, the same processes of the initiation and growth of the microcrack repeats themselves. Unlike the first event, the initial hydrogen concentration distribution ahead of the primary crack for the second event is higher as the result of hydrogen diffusion away from the crack tip. Therefore, it takes short time for hydrogen diffusion and accumulation to achieve the critical condition for microcrack initiation. On the macroscopic scale, the average crack growth rate is
increased. In other words, the gradual increase in the crack growth rate is the reflection of the gradual decrease of the microcrack initiation time. However, the crack growth rate can not increase without limit. The durations of the initiation time are related to the initial hydrogen concentration distribution immediately after the completion of an event of the microcrack initiation and growth and the previous initiation time. When the initiation time gradually decreases, the increase in the initial hydrogen concentration ahead of the primary crack tip gradually decreases. Finally, the initial hydrogen concentration approaches a limiting value. It is, thus, observed, on the macroscopic scale, the crack growth rate approaches a steady-state, or constant value.

Since the same kinetic processes is envisaged to take place for the incubation and transient periods, the division of these two periods is rather artificial; it is more reasonable to treat them as one rather than two different behaviors. It can be expected that the sum of the incubation and transient periods, under a given electrochemical potential, decreases with increasing stress intensity.
Another possible reason for the existence of the transient period may be that the crack, initially, does not propagate along the crack plane. The crack, first, propagates along slip planes off the primary plane, and, then, turns back and propagate along the primary crack plane. It has been observed that, for AISI 4340 steel of round, blunt notch under dynamic hydrogen charging condition, cracks propagate along slip planes (117). It is not known whether the same behavior occurs at a sharp crack tip as the stress distribution at the crack tip changes.

5.2 GROWING CRACKS

5.2.1 Sudden increase in stress intensity

The loading history in this case is similar to the previous cases except two differences. First, higher initial hydrogen concentration, relative to the critical hydrogen concentration for the microcrack initiation, exists in the vicinity of the tip of a growing crack than that existing in same region of a stationary crack. Second, the change in stress intensity is smaller compared to that
employed to the stationary cracks. The changes in the plastic zone at the crack tip is mild as the increase in the applied stress intensity is small; the change in the microstructure in the plastic zone is also mild. There is a small shift of the region of maximum hydrostatic tension away from the crack tip maximum hydrostatic tension is also small. The combining effects of these factors is a drastic decrease in the incubation and transient periods. Consequently, it was observed, under cathodic and open-circuit potentials, the crack could almost pick up the steady-state growth rate, characteristic of the higher applied stress intensity, immediately after the application of the higher stress intensity.

Under the anodic potential, the surface absorption of hydrogen is relatively low, and, thus, hydrogen flux away from the crack tip is decreased. A short duration of the incubation and transient periods is expected to be observed. It is noted that no clear dependence of the transient and incubation periods on the increase of the applied stress intensity. At the higher stress intensity, the surface absorption of hydrogen is enhanced due to the increase of the crack tip radius. However, the region of maximum hydrostatic tension is shifted further away from the crack tip. In other words, the driving force for
hydrogen diffusion contributed by the gradient of hydrostatic tension is reduced. It is, therefore, speculated that, over the range of stress intensity studied, the lack of the dependence of the incubation and transient periods on the change in the applied stress intensity is the result of the interplay of the above-mentioned two opposing factors.

5.2.2 Sudden decrease in stress intensity

The stress distribution ahead of the crack tip depends on loading history. When the applied stress intensity at the crack tip is reduced from $K_{i1}$ to a lower level $K_{i2}$, the stress distribution ahead of the crack tip is different from that resulted from loading an unstressed specimen to the stress intensity $K_{i2}$. The variation of the stress distribution ahead of the crack tip as the applied stress intensity is reduced from $K_{i1}$ to $K_{i2}$ is shown schematically in Figure 60. It is seen that compressive stress is introduced ahead of the crack tip when the applied stress intensity is reduced. The maximum compressive stress is 3... The presence of compression ahead of the crack tip is a result of straining of the released elastic stress surrounding the plastic zone. The presence of compressive
Figure 60 Schematic of the variation of stress distribution ahead of the crack tip as the applied stress intensity is reduced from $K_{11}$ to $K_{12}$. 
stress results in the decrease of maximum tension and maximum hydrostatic tension ahead of the crack tip. Also, the position of maximum hydrostatic tension is shifted from the crack tip. Consequently, the critical condition for microcrack initiation is destroyed, the crack, thus, stops growing. The crack can start to grow only when the critical condition is again satisfied. A microcrack must first be initiated at \( X \). As it propagates towards the crack tip, the stress ahead of the crack tip changes from compression to tension. Thereafter, the stress ahead of the crack tip becomes the same as that resulted from loading an unstressed specimen to the stress intensity \( K_{i2} \). The same processes of microcrack initiation and propagation repeat. Since the stress distribution ahead of the crack tip is independent of loading history after the initiation and propagation of the first microcrack, it is expected that the steady-state crack growth rate is independent of loading history.

For given \( K_{i1} \), the incubation time for microcrack initiation depends on \( K_{i2} \), or the reduction in \( K_i \), \( K_{i1} - K_{i2} \). As \( K_{i2} \) is decreased, the position maximum hydrostatic tension is shifted further away from the crack tip; maximum tension and maximum hydrostatic tension are lowered. The net effects are an increase of diffusion distance for
hydrogen from the crack tip to the region of maximum hydrostatic tension and an increase of the critical hydrogen concentration for microcrack initiation. Hence, the incubation time increases with the amount of reduction in applied stress intensity.

The effect of electrochemical potential is essentially the same as in previous cases. The more negative the electrochemical potential is, the higher is the adsorbed hydrogen concentration at the crack tip. Therefore, for a given loading history, the incubation and transient periods are shorter when the applied electrochemical potential is made more negative.

5.2.3 *Decrease of stress intensity at finite rates*
When the applied stress intensity at the tip of a growing crack is rapidly decreased, there is essentially no change in hydrogen distribution ahead of the crack tip. When the changing rate of stress intensity is reduced, there is time for hydrogen atoms to redistribute themselves to achieve new equilibrium. The slower the stress intensity is reduced, the faster hydrogen atoms can redistribute themselves to achieve a new equilibrium distribution. Therefore, the subcritical crack growth under stress
perturbation is a competition of hydrogen diffusion and the changing rate of stress intensity. When the changing rate of stress intensity is high, hydrogen has no time to catch with changing stress state at the crack tip; therefore, an incubation and transient period exist, after Ki2 is reached, before the crack can propagate at the steady-state rate characteristic of Ki2. When the changing rate of stress intensity is low, hydrogen redistribution can catch up with the changing stress distribution; consequently, as Ki2 is reached, the crack can immediately propagate at the steady-state rate characteristic of Ki2. For a given T, the time taken to complete the reduction in stress intensity, the incubation and transient periods apparently increase with the amount of change in stress intensity.

5.3 Dynamic Stress Corrosion Cracking

Experimental results obtained from Loading Schemes II, III, and IV exhibit the responses of growing cracks to different kinds of single perturbation. It has been found that, in all cases, the stress intensity perturbation stops the crack propagation. And the crack growth response is asymmetrical; given the same change in stress intensity, the crack growth responds differently depending the change in
stress intensity is a decrease or an increase. It is that the decrease in stress intensity has stronger effect on the crack growth behavior. On the basis of these observations, the crack growth behaviors under cyclic stress intensity can be understood. Over the range of frequency and stress intensity amplitude employed in this study, fatigue crack growth rates in air are relatively low compared with the steady-state stress corrosion crack growth rate at the mean stress intensity, therefore, it can be assumed no contribution to crack growth from fatigue.

Changes in applied stress intensity result in the dissolution of the critical combination of hydrogen concentration and stress state ahead of the tip of growing cracks. More time must be taken for hydrogen diffusion and accumulation to regain the critical condition for fracture. Therefore, dynamic stress corrosion crack growth rates are smaller than the crack growth rate obtained under sustained loading at the mean stress intensity. For a given waveform and stress intensity amplitude, the rate of stress intensity variation increases with increasing cyclic frequency. It gets more difficult for hydrogen diffusion and accumulation to keep up with the changing stress state ahead of the crack tip; the dynamic stress corrosion crack growth, therefore, decreases with increasing cyclic
frequency. Similarly, for a given waveform and frequency, the rate of variation of stress intensity increases as the stress intensity amplitude increases. Consequently, the dynamic stress corrosion crack growth rate decreases with increasing stress intensity amplitude.

It is observed that, for a given stress intensity amplitude and frequency, the dynamic stress corrosion crack growth rate obtained from cyclic square loading is higher than those obtained from sawtooth loadings. In cases of square waveform, there is holding at maximum and minimum stress intensities. There is no change in stress distribution ahead of the crack tip at either maximum or minimum stress intensity, it is easier for hydrogen diffusion and accumulation to follow the stress state. However, stresses ahead of the crack tip keeps changing when sawtooth waveform is imposed. Under the latter condition, the critical condition for fracture is more difficult to achieve; hence, the dynamic stress corrosion crack growth rate is lower under sawtooth waveforms.

In cases of positive sawtooth waveform, during each cycle, stress intensity increases at a lower rate when it is decreased. The opposite is true for negative sawtooth waveform. It is known from experimental results of Loading
Schemes II, III, and IV, the crack growth response is significantly influenced by the decrease in stress intensity; and when the decreasing rate of stress intensity is reduced, the incubation and transient periods become shorter. Further, the crack growth response is less sensitive to the rate of change of stress intensity when it is increased. Therefore, in each cycle, it is the part that the stress intensity being reduced controls the crack growth behavior under cyclic sawtooth waveforms. For negative sawtooth waveform, it is easier for hydrogen diffusion and accumulation since the decreasing rate of stress intensity is much lower. As a result, the dynamic stress corrosion crack growth rate is higher when negative waveforms are imposed.
Chapter VI
CONCLUSIONS

The effect of stress intensity perturbation on the crack growth behavior of high strength AISI 4340 steel in 3.5% sodium chloride solution are summarized below:

1. Upon sudden application of a constant stress intensity, which is greater than the threshold stress intensity, to a stationary crack, steady-state crack growth rate is achieved only after an incubation period of no crack growth and a transient period of time-dependent crack growth rate.

2. At a given electrochemical potential, the time taken for the crack to achieve a steady-state crack growth rate decreases when the applied stress intensity is increased. For a given stress intensity, the time taken for the crack to achieve a steady-state crack growth rate is decreased as the electrochemical potential is made more negative.

3. Incubation and transient periods were found to exist when the applied stress intensity at a growing crack tip
was suddenly changed. Under cathodic and open-circuit potential conditions, steady-state crack growth rates were achieved almost immediately upon imposition of a step increase in stress intensity.

4. In case of a step decrease in applied stress intensity at a growing crack tip, the time taken for the crack to achieve a steady-state growth rate increases with increasing size of the step. For a given change in stress intensity, the time taken for the crack to achieve the steady-state growth rate was found to decrease as the applied potential was made more negative.

5. When the decreasing rate of the applied stress intensity was reduced, the crack took shorter time to achieve a steady-state growth rate. When the decreasing rate of stress intensity was less than a critical value, the crack could grow immediately at the steady-state rate at the completion of reduction in stress intensity. The critical time period increased with the magnitude of reduction in stress intensity.

6. Under low amplitude and low frequency cyclic loading conditions, the crack growth rates were lower than that obtained at mean stress intensity under sustained loading condition. The crack growth rate decreased with increasing frequency and/or increasing amplitude of cyclic loading.
7. For given stress intensity amplitude and frequency, the crack growth rate was higher under square cyclic loading than under sawtooth cyclic loading. And, the crack growth rate was higher under negative sawtooth cyclic loading than under positive sawtooth cyclic loading.

8. Subcritical crack growth behaviors under different kinds of stress intensity perturbation have been explained in terms of hydrogen embrittlement, in which the rate-limiting process is hydrogen diffusion in the non-uniform stress field in the plastic zone ahead of the crack tip.
REFERENCES


