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Tsai, Wen-Ta

A STUDY OF CORROSION FATIGUE CRACK GROWTH IN IRON-CHROMIUM-NICKEL ALLOYS

The Ohio State University

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A STUDY OF CORROSION FATIGUE CRACK GROWTH IN 
FE-CR-NI ALLOYS

DISSERTATION

Presented in Partial Fullfillment of The Requirement for 
the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By 
Wen-Ta Tsai, B.S., M.S.

* * * * *

The Ohio State University
1983

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DEDICATION

This dissertation is dedicated to my entire family:
To my parents who enabled me to attend college.
To my sisters and brothers for their encouragement.
To my loving wife Huan-Li, whose patient support
and encouragement helped make it all possible.
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96. Effect of chromium content on the anodic polarization behavior of Fe-Cr-Ni alloys in deaerated water containing 0.01 N Na$_2$SO$_4$ at 288 C.
Environmental cracking that has occurred in nuclear power generating equipment can result in an unscheduled shutdown of the whole plant. Some of the cracking incidences that have happened in nuclear power generating plants can be found in the open literature (1-4). The forced outage due to material failures will cause a lack of plant availability (5). It has been estimated that the loss of 1000 MW of nuclear power during an outage would cost as much as one million dollars a day (2-3). As a result of the economic loss, a strong incentive exists to study the cracking problems.

Environmentally caused cracking is generally classified into three categories: stress corrosion cracking (SCC), corrosion fatigue (CF) and hydrogen-assisted cracking. Incidences due to one of the above nature have been observed in the failure of condensers; turbine discs, rotors and blades; nuclear reactor piping and steam generator tubing, etc. The alloy/environment systems concerned have ranged from low strength ductile alloys in aqueous environments to
high strength alloys in gases, with either static or dynamic stress conditions.

Since most of the structural materials are potentially susceptible to corrosion fatigue, the objective of this study was to investigate the corrosion fatigue crack growth (FCG) behavior in various materials used in nuclear power generating equipment in simulated conditions. Three different kinds of materials were investigated in this study: Type 403 stainless steel (S.S.), Inconel 600, and Type 304 stainless steel. Although it was not the purpose of this study to investigate the stress corrosion cracking behavior, the correlation between stress corrosion and corrosion fatigue has been formulated in ductile material/environment systems.

Type 403 stainless steel is primarily used for the fabrication of steam turbine blades in electric power generating systems. These blades are subjected to cyclic stresses under operating conditions. Sodium chloride and sodium hydroxide are common impurities in the steam turbine systems, and the buildup of local concentrations of these impurities on the blade surfaces is a well known phenomenon (6). Thus, fatigue-associated failures in these corrosive environments are not uncommon.
The piping materials used in Boiling Water Reactors (BWR) and Pressurized Water Reactors (PWR) are primarily fabricated from Type 304 stainless steel. The tubing materials used in PWR steam generator are mainly made of Inconel 600. These pipes and tubes in nuclear reactor structures are subjected to various types of cyclic loadings such as: pressure fluctuations, secondary water flow, thermal cycling and the startup-shutdown process, and thus they are potentially susceptible to fatigue failures. Corrosion fatigue in Inconel 600 and Type 304 stainless steel has been extensively studied in aqueous environments at temperature below 140 C, however, very limited work on corrosion fatigue in these materials has been performed in high temperature and high pressure PWR and BWR environments. Therefore, it is of great worth to investigate the cracking behavior in these materials in BWR and PWR environments and under cyclic loading conditions.

Since in most structural materials flaws are likely to be present, the propagation behavior of these subcritical cracks is the most important to the cracking problems. Therefore, the propagation stage rather than the initiation stage was studied. Due to the different emphases of interest, the objectives of the investigation of corrosion fatigue crack growth in the Fe-Cr-Ni ternary alloys in this study were divided into the following three parts:
1. Inhibition of corrosion fatigue crack growth in Type 403 stainless steel in concentrated sodium chloride and sodium hydroxide solutions.

2. Corrosion fatigue crack growth in Inconel 600 in PWR environments, and

3. The effect of potential on the corrosion fatigue crack growth in Type 304 stainless steel in BWR environments.

This dissertation is divided into three main sections. The literature survey provides the necessary background information. The section entitled "Experimental Details" describes the materials, the experimental apparatus, and the experimental procedures used in the course of this investigation. The results and discussion are included in the third main section and the conclusion of this study follows.
Chapter II
LITERATURE SURVEY

The following review is intended to give some background information about the environmentally-caused cracking in the Fe-Cr-Ni alloys, which is related to the interest of this study. Since the crack growth rate is reported as a function of the stress intensity factor range (ΔK), a brief summary of linear elastic fracture mechanics (LEFM) will be first introduced in this review. The concept and theory of fatigue crack propagation will be included in the second part. In part three the effect of environment on the fatigue crack growth rate will be discussed. Some background about stress corrosion cracking and hydrogen embrittlement will be described in part four. Finally, the behaviors of corrosion fatigue and stress corrosion cracking in Type 403 stainless steel, Inconel 600, and Type 304 stainless steel will be briefly presented in parts five, six, and seven, respectively.
2.1 Brief Summary of LEFM

The development of fracture-mechanics methodology offers considerable promise in improving our understanding of fatigue-crack initiation, fatigue-crack propagation, and unstable crack propagation, and in solving the problem of designing to prevent failures caused by fatigue. Linear-elastic-fracture-mechanics technology is based on an analytical procedure that relates the stress-field magnitude and distribution in the vicinity of a crack tip to the nominal stress applied to the structure, to the size, shape, and orientation of the crack or crack-like imperfection, and to the material properties. The fundamental basis for the development of linear fracture mechanics is Griffith (7) Theory.

2.1.1 Griffith Theory

Griffith noted that when a crack is introduced into a stressed plate of elastic material, a balance must be maintained between the decrease in potential energy and the increase in surface energy resulting from the presence of the crack. By using the energy approach and the stress analysis of Inglis (8) for the case of an infinitely large plate containing a through-thickness crack of length 2a, the total elastic energy of the system, $U$, may be given by
\[ U = U_0 - \frac{\pi \sigma^2 a^2}{E} + 4\pi \gamma_e \]  

where \( U_0 \) = elastic energy of the uncracked plate,  
\( \sigma \) = applied tensile stress,  
\( \gamma_e \) = elastic-surface energy of the material, and  
\( E \) = Young's modulus of the material.  

At equilibrium condition, the crack extension criterion is  

\[ \frac{\pi \sigma^2 a}{E} = 2\gamma_e \]  

The left-hand side has been designated the energy-release rate, \( G \), and represents the elastic energy per unit crack surface area that is available for infinitesimal crack extension. The right-hand side of Equation 2 represents the material's resistance to crack extension, \( R \).  

Griffith fracture criterion is valid for ideally brittle material (9). Since most materials exhibit plastic deformation, Equation 2 was modified by Irwin (9) as follow:  

\[ G = 2(\gamma_e + \gamma_p) \]  

where \( \gamma_p \) is the plastic-strain work. A similar modification of Griffith Theory was proposed by Orowan (10) at about the same time. He also suggested that Equation 2 be modified to include the energy of plastic deformation in the fracture process.
2.1.2 **Stress Analysis of Cracks**

Since crack extension and corrosion attack would occur in the highly stressed region at the crack tip, the stress distribution in the crack tip region should be considered. The stress fields near crack tips may be divided into three basic types of loading that involve different crack surface displacements (11), as shown in Figure 1.

The opening mode, Mode I, is characterized by the direct separation of the crack surfaces symmetrically with respect to the plane containing the crack. The sliding mode, Mode II, is characterized by the displacement in which the crack surfaces slide over one another in a direction perpendicular to the leading edge of the crack. The tearing mode, Mode III, is associated with local displacement in which the crack surfaces move relative to one another and parallel to the leading edge of the crack. In any problem the deformations at the crack tip can be treated as one or a combination of these local displacement modes. Moreover, the stress field at the crack tip can be treated as one or a combination of the three basic types of stress fields. Since Mode I is the most common type of deformation in actual engineering situations, only this mode will be considered for the present discussion. However, the general discussion will be applicable to the other two modes as well.
Figure 1  The three basic modes of crack surface displacement. (Reference 11)
The stress and displacement fields associated with the opening mode, Mode I, in an isotropic elastic body are given by (11-13)

\[
\sigma_x = \frac{K_I}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \left[ 1 - \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right]
\]

\[
\sigma_y = \frac{K_I}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \left[ 1 + \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right]
\]

\[
\sigma_{xy} = \frac{K_I}{\sqrt{2\pi r}} \sin \frac{\theta}{2} \cos \frac{\theta}{2} \cos \frac{3\theta}{2}
\]

(4)

\[
u = \frac{K_I}{8\mu \sqrt{2\pi}} \left[ (2\chi - 1) \cos \frac{\theta}{2} - \cos \frac{3\theta}{2} \right]
\]

\[
\tau = \frac{K_I}{8\mu \sqrt{2\pi}} \left[ (2\chi + 1) \sin \frac{\theta}{2} - \sin \frac{3\theta}{2} \right]
\]

For plane strain condition:

\[
\chi = 3 - 4\nu
\]

\[
\sigma_z = \nu(\sigma_x + \sigma_y)
\]

\[
w = 0
\]

For plane stress condition:

\[
\chi = \frac{3 - \nu}{1 + \nu}
\]

\[
\sigma_z = 0
\]

\[
w = -\frac{\nu}{E} \int (\sigma_x + \sigma_y) \, dz
\]
r and $\theta$ are the coordinates (Figure 2); $\mu$ is the shear modulus; and $\nu$ is the poisson's ratio. Higher order terms of $r$ have been neglected in Equation 4.

Equation 4 shows that the distribution of the elastic-stress and deformation fields in the vicinity of the crack tip are invariant in all components subjected to a given mode of deformation and that the magnitude of the elastic-stress field can be described by single-term parameter $K_I$, the stress intensity factor.

Crack initiation and subcritical crack propagation may be caused by fatigue, by stress corrosion cracking or by corrosion fatigue. All these modes of crack initiation and subcritical crack propagation are localized phenomena that depend on the stress-field intensity at the tip of the notch or crack. Since the stress field in the vicinity of a crack is only governed by the magnitude of the stress intensity factor, it seems most appropriate to use $K$ to characterize the mechanical driving force.

For most engineering materials, some plastic deformation will occur in the region near the crack tip. If the zone of plastic deformation is small in comparison with the crack size and with other planar dimensions of the body, the overall stress distribution in the body will not be
Figure 2 Coordinates and stress components in the crack tip stress field. (Reference 11)
seriously disturbed. The elasticity solutions (Equation 4) will then represent a reasonable approximation of the stress and displacement field near the crack tip. With the assumption of limited plasticity, the crack tip stress intensity factor, $K$, which is defined by linear elasticity, may be used to characterize the mechanical driving force for practical engineering materials which contain cracks. Dimensional analysis of Equation 4 indicates that the stress intensity factor must be linearly related to stress and the square root of a characteristic length. The general form of the stress intensity factor is given by

$$K_I = f(g)\sigma \sqrt{\alpha}$$

(5)

where $f(g)$ is a parameter that depends on the specimen and the crack geometry. Various types of specimens and loading configurations may be used to study the effects of environment on subcritical crack growth. The more popular specimens are those containing through-thickness cracks. Depending on the type of specimen and the method of loading, the stress intensity factors may be separated into three groups:

1. constant load, increasing $K_I$ specimens,
2. constant displacement, decreasing $K_I$ specimens, and
3. constant $K_I$ specimens.
K₁ calibrations for the various common types of test specimens and loading configurations have been determined and are available in the fracture mechanics literature (11, 14-16). More general and fundamental information about the linear elastic fracture mechanics can be found in various fracture mechanics textbooks (17-20).

2.2 CONCEPT AND THEORY OF FATIGUE CRACK PROPAGATION

The fatigue life of a structural component may be divided into three stages: 1) fatigue crack initiation, 2) fatigue crack propagation, and 3) fracture. Several models (21-22) have been proposed for the mechanism of fatigue crack initiation without the assistance of aggressive environments. Once a fatigue crack is initiated, the fatigue life of the structural component is dependent upon the propagation rate of the fatigue crack. As soon as the crack grows to a critical length where the stress intensity factor reaches the value of the fracture toughness K_c (or K_{IC}) of the materials, the structural component will fail by fracturing. The initiation and fracture stages are not within the scope of interest of this study, therefore, the following discussion will focus on fatigue crack propagation only.
2.2.1 Mechanism of Fatigue Crack Growth

A fatigue crack, once started, can grow by a mechanism of reversed slip (19). Several stages of fatigue crack growth are shown in Figure 3. When tensile stress is applied to a sharp crack, a slip may occur along a favorable slip plane in the direction of maximum shear stress. Due to that slip the crack opens and extends in length (stages 1 and 2). A new slip can now occur on another favorable slip plane (stage 3). Work hardening and increasing stress will finally activate other parallel planes, which leads to a blunt crack tip (stage 4). During the rising load part of the cycle the crack has propagated by an amount \( \Delta a \). Meanwhile, a small plastic zone has been developed in the tip region by the application of a stress intensity factor of magnitude \( K \). During the load release period of the cycle, the surrounding elastic material will exert compressive stresses on the plastic region. These compressive stresses will cause a reversed plastic deformation, which will close and resharpen the crack tip (stage 5). These repeated opening and closing processes at the crack tip result in the growth of the crack.
Figure 3 Possible model for fatigue crack growth.
(Reference 9)
2.2.2 Fatigue Crack Growth Law

It has been indicated by Paris (23) that the rate of fatigue crack growth in a given material depends on the range of variation of the stress intensity factor, $\Delta K$. He also proposed a famous power law for the fatigue crack propagation behavior, which is given as follows (23):

$$\frac{\Delta a}{\Delta N} = C (\Delta K)^n$$

where $C$ is a parameter depending on the material property and the loading condition, $n$ is the exponent which can be evaluated from the slope of a log-log plot of the test data. A schematic illustration of fatigue crack growth rate is given in Figure 4. At intermediate stress intensities, the crack growth rate can fairly well be represented by Equation 6. This is shown as the dashed line in Figure 4. At low stress intensities, a fatigue crack growth threshold, $K_0$, is observed. If this threshold is considered, the fatigue crack growth rate law becomes (24):

$$\frac{\Delta a}{\Delta N} = C (\Delta K - K_0)^n$$

At very high $\Delta K$ level, Paris law was further modified. Foreman (25) considered the effect of the critical stress intensity factor $K_c$ (or $K_{1c}$) and $R$, the ratio of minimum to maximum stress, on the fatigue crack growth rate, and he gave the following expression:

$$\frac{\Delta a}{\Delta N} = C (\Delta K)^n / ((1-R)K_c - \Delta K)$$
Figure 4 Schematic illustration of fatigue crack growth rate law. (Reference 24)
Combining the above three equations, Speidel (24) gave a general expression for the fatigue crack growth rate law as follow:

\[ \frac{\Delta a}{\Delta N} = C(\Delta K - K_f)^n / (1 - B) \]  

(9)

This equation can describe the sigmoidal shape of the \( \Delta a/\Delta N \) versus \( \Delta K \) curve (Figure 4) which is often observed in high strength materials.

Many other equations have been derived to describe the fatigue crack growth rate law. However, it has been found that the relationship shown in Equation 6 can represent the behavior of a large number of materials, and Equation 6 is the most accepted equation.

2.3 PROPAGATION OF CORROSION FATIGUE CRACKS

The previous section dealt with the crack propagation aspect of fatigue failure without the presence of aggressive environments. However, the majority of observed fatigue failures are, in fact, assisted by the corrosive media. In other words, most fatigue failures are results of corrosion fatigue -- the combined action of cyclic loading and corrosive environments. The service life of a structural component which is subjected to cyclic loading is influenced
by many factors. Some of the factors affecting the fatigue life are summarized in the following section (25).

2.3.1 Variables Affecting Fatigue Crack Growth

The propagation rate of fatigue cracks depends on the stress conditions, environments, and the material properties. Some of the most significant variables indicated by Wei and Speidel (25) are listed as follows:

Mechanical Variables:

1. Maximum stress or stress intensity factor, $\sigma_{\text{max}}$, or $K_{\text{max}}$.
2. Cyclic stress or stress intensity range, $\Delta \sigma$ or $\Delta K$.
3. Stress ratio, $R$.
4. Cyclic loading frequency, $f$.
5. Cyclic load wave-form (constant amplitude loading).
6. Load interaction in variable amplitude loading.
9. Crack size and shape, and their relation to component size and geometry.

Metallurgical Variables:

1. Alloy composition.
2. Distribution of alloying elements and impurities.
3. Microstructure and crystal structure.
5. Mechanical working.
6. Preferred orientation of grains and grain boundaries.
7. Mechanical properties (strength, fracture toughness, etc.).

Environmental Variables:
1. Temperature, T.
2. Types of environments: gaseous, liquid, liquid metal, etc.
3. Partial pressure of damaging species in gaseous environments, p_i.
4. Concentration of damaging species in aqueous or other liquid environments, C_i.
5. Electrochemical potential, φ.
6. pH.
7. Viscosity of the environment, η.
8. Coating, inhibitors, etc.

The fatigue crack growth rate law as discussed in the previous section has indicated that the value of $\Delta a / \Delta N$ in inert environments depends on the stress intensity factor
range (ΔK), stress ratio (R), and material properties. When the environment comes into action, the fatigue crack growth behavior becomes more complicated. Consequently, the fatigue crack growth rate will be a function of all the variables mentioned, namely:

\[
a/N = g(K, R, f, T, C_i, \phi, \ldots) 
\]

(10)

From the viewpoint of engineering applications, it is desirable to know the influences all these variables may have on the fatigue behavior in a material. However, such investigation is expensive and unnecessary. More practically, the study of corrosion fatigue behavior is only limited to a few variables, for example, frequency, heat treatment, and electrical potential, etc.

As just mentioned above, the fatigue crack propagation is a complicated phenomenon when corrosive environments are present, because stress corrosion cracking or hydrogen embrittlement may participate in the cracking processes. When the environmental effect becomes important, a time-dependent, rather than cycle-dependent, phenomenon may be observed. Depending upon the type of corrosion fatigue crack growth behavior, the material/environment systems have been classified into three patterns. Since corrosion fatigue cracks may propagate when stress intensity factors are below the stress corrosion cracking threshold, \( K_{I_{SCC}} \), the
corrosion fatigue behaviors also have been classified as below $K_{I_{SCC}}$ or above $K_{I_{SCC}}$ corrosion fatigue. More detailed discussion on the types of corrosion fatigue will be presented in the following section.

2.3.2 Classification of Corrosion Fatigue Crack Growth Behavior

Speidel et al (26) have characterized the corrosion fatigue crack growth rate versus stress intensity plot in three stages, as illustrated schematically in Figure 5. The crack growth rate in Region I at low $\Delta K$ values is extremely dependent on stress intensity. There exists a threshold stress intensity below which cracks in the environment in question do not propagate under cyclic-stress fluctuations. This threshold stress intensity, in analogy to $K_{I_{SCC}}$, is environment-dependent and may be different from the value of $K_0$ (Figure 4), because the latter is a threshold in inert environments. In Region II of the da/dN versus $\Delta K$ curve, the corrosion fatigue crack growth rate often depends strongly on the environment, but its stress dependence is considerably reduced. In some cases, the crack growth rate is completely independent of $\Delta K$ over a certain stress intensity range. For example, Walker et al (27) have reported that a plateau in Region II has been observed in
Figure 5 Schematic representation of the influence of stress intensity on the growth rate of corrosion fatigue cracks. (Reference 26)
titanium/salt water system. According to Speidel et al. (26), three types of behavior have been observed in Region III depending on the specific metal-environment couple as illustrated in Figure 5. They are:

1. Divergence from the inert environment curve, i.e.; further crack growth acceleration (A in Figure 5).
2. The aggressive environment and inert environment curves become parallel (B in Figure 5).
3. Convergence of the aggressive environment and inert environment curves to form a common curve (C in Figure 5).

On the other hand, McEvily and Wei (28) have characterized the corrosion fatigue crack growth response in terms of three general patterns of behavior, as illustrated in Figure 6. The first type of behavior (Type A) represents those material/environment systems where the enhancement of fatigue crack growth rate results from the synergistic actions of corrosive agents and cyclic loading, which is sometimes called "true corrosion fatigue" (26). This behavior pattern is typified by that of the aluminum/water system (29). Type B represents those systems where the crack growth is enhanced by an environmentally assisted sustained load crack growth component. The typical behavior of this type is found in hydrogen/steel system (30,31). Type
Figure 6 Types of corrosion fatigue crack growth behavior. (Reference 28)
C represents the behaviors of a broad range of material/environment systems.

Corrosion fatigue crack propagation behavior has also been characterized on the basis of the maximum stress intensity factor, $K_{\text{Imax}}$. Since $K_{\text{ISCC}}$ for a material/environment system defines the plane-strain $K_I$ value above which stress-corrosion crack growth can occur under static loads, the corrosion-fatigue behavior for the material/environment system could be altered when the maximum value of $K_I$ in a load cycle becomes greater than $K_{\text{ISCC}}$. Consequently, the corrosion-fatigue behavior has been divided into below-$K_{\text{ISCC}}$ and above-$K_{\text{ISCC}}$ types (32-35). However, a recent study conducted by Ford and Silverman (36) has indicated that $K_{\text{ISCC}}$ for ductile alloy/aqueous environment systems can not be regarded as a system constant for components undergoing dynamic loading. They found that $K_{\text{ISCC}}$ will decrease with dynamic loading. Therefore, it is not appropriate to characterize the corrosion fatigue as below-$K_{\text{ISCC}}$ or above-$K_{\text{ISCC}}$ behaviors, since the value of $K_{\text{ISCC}}$ depends on the loading conditions.
2.3.3 **Superposition Model and Competition Model for Corrosion Fatigue Crack Growth**

Quantitative studies of corrosion fatigue crack growth have led to the development of superposition (31) and competition (37) models. Fatigue crack growth in metals in an aggressive environment has generally been considered to be composed of two components -- a mechanical component and an environmental component. The mechanical component, which is cycle dependent, represents the rate of fatigue crack growth in the absence of the influence of an external environment. The environmental component, which is time dependent, is determined from experimental crack growth data under sustained loading in the appropriate environment and from the fatigue-load profile. Based on this concept, Wei and Landes (31) and Bucci (38) have proposed that fatigue crack growth rate in an aggressive environment is simply equal to the algebraic sum of the above two components, if they are independent of each other. The superposition model is, thus, expressed as follow:

\[
\frac{da}{dN}_c = \frac{da}{dN}_r + \frac{da}{dN}_e
\]

or

\[
\frac{da}{dN}_c = \frac{da}{dN}_r + \int \frac{da}{dt}_e \, dt
\]

where \(\frac{da}{dN}_c\) is the corrosion fatigue propagation rate, \(\frac{da}{dN}_r\) is the cycle dependent fatigue crack propagation
rate in inert environments, $\frac{da}{dN}_E$ is the environmental rate of attack, $\frac{da}{dt}_E$ is the time-based environmental component and $\gamma (=1/frequency)$ is the period of one cycle. A convenient way to examine the effect of frequency is to rewrite Equations 11 and 12 in their time-based equivalent (32-33):

$$\frac{da}{dt}_c = \frac{da}{dt}_E + f \times \frac{da}{dN}_r \quad (13)$$

Equation 13 is obtained by multiplying Equations 11 and 12 by the frequency, $f$, of the applied load. The superposition model is applicable to the Type B behavior (28) of Figure 6, where the mechanical component is independent of the environmental component, and $\frac{da}{dt}_E$ is essentially the stress corrosion cracking rate, $\frac{da}{dt}_{sc}$.

Since the superposition model was first proposed, it has been drawn several arguments against it (18,26,36,39-41). For example, McEvily et al (28) has indicated that this model is grossly oversimplified, but that it is of interest as first order approximations.

In the superposition model, the two terms are assumed to be independent, and $\frac{da}{dN}_r$ is always obtained in inert environments. However, when the environment is more aggressive, the cycle dependent crack growth rate becomes higher than $\frac{da}{dN}_r$, illustrated as Type C in Figure 6. In
order to apply the superposition model to Type C behavior, it has been modified (41) by replacing $\frac{da}{dN}_r$ with the true corrosion fatigue crack growth rate, $\frac{da}{dN}_{tCF}$. Thus, Equation 13 becomes (41)

$$\frac{da}{dt}_c = \frac{da}{dt}_e + f \times \frac{da}{dN}_{tCF} \quad (14)$$

Kawakubo et al. (41) have shown that Equation 14 is no longer a linear summation model, since $\frac{da}{dN}_{tCF}$ is a function of frequency and it includes the synergistic effect between the cyclic stresses and the aggressive environment.

More recently, Austen and Walker (37) have proposed that fatigue and stress corrosion crack growth processes are mutually competitive, not additive as in the Wei and Landes model, and that the crack will propagate at the fastest available rate pertinent to the prevailing stress intensity. This implies that corrosion fatigue crack growth curves can be constructed by combining fatigue (or true corrosion fatigue) and stress corrosion plots and simply taking the fastest rate throughout. Austen and Walker have reported that the competition model works very well to predict the corrosion fatigue crack growth behavior in the 835M30 steel/3.5% NaCl system (37).

The effect of environment on the fatigue crack growth rate can be easily understood by examining either the $\frac{da}{dN}$...
vs $\Delta K$ or $da/dt$ vs $f$ curves. If fatigue cracks propagate in a cycle-dependent manner, then, the fatigue propagation rate $da/dN$ at each $\Delta K$ will have the same value for different cyclic frequencies, and the time-based $da/dt$ vs $f$ curve will be a straight line having a gradient of unity. The value of $da/dt$ will decrease one order of magnitude for each order of magnitude decrease in frequency for cycle-dependent behavior. On the other hand, if the time-dependent environmental attack becomes important, then the value of $da/dN$ for each $\Delta K$ will increase with decreasing frequency, and the $da/dt$ vs $f$ curve will deviate from the straight line with unit gradient. An example of the $da/dt$ vs $f$ curves for 4340 steel is shown in Figure 7 (32).

On the other hand, the effect of frequency on the corrosion fatigue crack growth rate behavior may also be determined from the $da/dN$ vs $f$ plot, as illustrated in Figure 8 (38). In this case, the cycle-dependent behavior is illustrated by a horizontal line, while the time-dependent behavior is depicted by a straight line with a slope of unity in the log-log plot.
Figure 7 Corrosion fatigue crack growth rate behavior of 4340 steel. (Reference 32)
Figure 8 Effect of frequency on the growth rate of fatigue crack in Nimonic 105 in water. (Reference 39)
2.4 Stress Corrosion Cracking and Hydrogen Embrittlement

Stress corrosion cracking (SCC) and hydrogen embrittlement may both be involved in corrosion fatigue processes. Two mechanisms are generally accepted as causes of the stress corrosion cracking phenomenon: a) dissolution of the metal in the path of the crack, and b) hydrogen-assisted cracking (hydrogen embrittlement) from corrosion-generated hydrogen. Although hydrogen embrittlement may participate in the processes of corrosion fatigue and stress corrosion cracking, it may also take place without the involvement of these two processes. Hence, stress corrosion cracking and hydrogen embrittlement will be discussed separately in this section.

2.4.1 Phenomenology and Mechanism of Stress Corrosion Cracking

Stress corrosion cracking is a process caused by the conjoint action of stress (applied or residual), environment and microstructure, as illustrated in Figure 9. Like the corrosion fatigue process, SCC can be divided into three regions: 1) crack initiation, 2) crack propagation, and 3) final fracture. A schematic diagram showing the possible SCC sequence for high strength steel is illustrated in Figure 10 (42).
Figure 9 Venn diagram showing the cause of stress corrosion cracking.
Figure 10 The sequence of events which could occur in SCC testing of a smooth specimen. (Reference 42)
The methods commonly used to study stress corrosion cracking are constant extension rate tests (CERT). The CERT results may be suitable for making qualitative comparisons between environments and materials (43), however, they may not be able to predict the service life of a structural component quantitatively. Therefore, the use of fracture mechanics is preferred. The dependence of subcritical crack growth rate \( \frac{da}{dt} \) on the stress intensity factor \( K \) is shown in Figure 11. In general, the results suggest that the stress corrosion crack growth rate behavior as a function of the stress intensity factor can be divided into three regions. In Region I, the rate of stress corrosion crack growth is strongly dependent on the magnitude of stress intensity factor, \( K \). The behavior in Region I exhibits a stress intensity factor below which cracks do not propagate under sustained loads for a given material/environment system. The threshold stress intensity factor corresponds to \( K_{isc} \). In Region II, \( \frac{da}{dt} \) is insensitive to \( K \). In such case, the primary driving force for crack growth is not mechanical in nature but is related to other processes such as mass transport and diffusion processes. At still higher stress intensities the crack growth rate in Region III increases rapidly with \( K \) as the value of \( K \) approaches the \( K_c \) of the material.
The slip-dissolution mechanism (47-49) is the most widely accepted model for stress corrosion cracking. Crack propagation takes place through the repetition of the following three steps, as shown in Figure 12: 1) Fracture of the protective film on the metal surface due to straining, 2) bare surface dissolution, and 3) repassivation. A similar model called the tarnish-rupture (or brittle film) model was also developed (50-52). According to this model, cracking occurs discontinuously by the repeated formation and rupture of the tarnish layer. The essential feature is that the oxide grows into the metal and that cracking is confined to this brittle layer, the crack rapidly becoming arrested by plastic deformation when it enters the ductile substrate. Once the crack is arrested, further tarnish growth occurs at the tip, until, at a critical thickness, the oxide again undergoes fracture.

Hydrogen embrittlement is generally considered as a mechanism when it is engaged in the corrosion fatigue or stress corrosion cracking processes. However, Thompson and Bernstein (53) have suggested that it be regarded as a phenomenon rather than a mechanism. Understanding of the role of metallurgical variables in hydrogen embrittlement has proven significant in recent years. An excellent review can be found in Reference 53. But the cracking process in
Figure 11 Schematic illustration of the functional relationship between stress intensity factor (K) and subcritical crack growth rate (da/dt).
Figure 12 Schematic figure showing crack propagation in slip-dissolution model. (Reference 41)
which hydrogen is involved is still not quite understood. Only a brief survey will be presented in the following subsection.

2.4.2 The Behavior and Effect of Hydrogen

The presence of hydrogen may come from several different sources. In the first case, hydrogen may be present in a material as a result of processing, for example, solidification or heat treatment in a hydrogen atmosphere. The simplest case is that H₂ molecules adsorb onto the surface, dissociate there, and are absorbed into the metal as dissolved hydrogen (H). The second source is H⁺ in solution, for example, in an acidic environment or as a result of a hydrolysis reaction (54). The third case is a chemical reaction in which a hydrogen-containing molecule reacts with the metal to release hydrogen (55-56).

In most cases, hydrogen-assisted cracking requires the transport of hydrogen. There are various possible paths for such hydrogen transport processes. Some of them are as follows: lattice diffusion, dislocation motion, or short-circuit diffusion along grain boundaries or dislocations. There are also several locations where the presence of hydrogen can cause fracture behavior. These include the
lattice itself, as well as grain boundaries, incoherent and coherent precipitates, voids and dislocations (53). The results of fracture may appear as cleavage cracking, intergranular cracking or ductile failure. The hydrogen processes summarized by Thompson and Bernstein (53) are illustrated in Figure 13.

The mechanism which leads to hydrogen embrittlement is not well known. However, various models have been proposed to account for the hydrogen-assisted cracking phenomenon. Among those which have been proposed are surface energy reduction models and decohesion models. Fetch (57) considered that hydrogen embrittlement could be interpreted as resulting from a reduction of surface energy by adsorbed hydrogen. In the Griffith model (7) of brittle cracking in a purely elastic body, the nominal fracture stress is proportional to the square root of the surface energy (Equation 2), so that a reduction in surface energy by adsorption would lead to increased brittleness. The decohesion model (58-60) is based on the concept that hydrogen reduces the cohesive force in the metal lattice. Such an effect could lead to a loss of tensile ductility. Other models, such as the pressure mechanism model (61-62), the dislocation mobility model (63) and the Hydride formers model (64-65) are extensively discussed in a review paper by Hirth and Johnson (66).
Figure 13 Summary of hydrogen processes. (Reference 53)
2.5 **CORROSION FATIGUE AND STRESS CORROSION CRACKING IN TYPE 403 STAINLESS STEEL**

2.5.1 **Corrosion Fatigue in Type 403 Stainless Steel**

Very limited investigations have been conducted on corrosion fatigue and stress corrosion cracking in Type 403 stainless steel in simulated steam turbine environments. Shalaby (67) studied fatigue crack initiation in Type 403 stainless steel in aqueous solutions. The environments investigated were: air, distilled water, sodium chloride solution, sodium sulphate solution, sodium phosphate solution, sodium hydroxide solution, and sodium silicate solution. He found that the fatigue life in aqueous environments may be reduced by an order of magnitude as compared with that obtained in air tests. The effect of heat treatment on the fatigue crack growth rate in Type 403 stainless steel in water was studied by Speidel (68). He found that the tempering temperature had a pronounced effect on the corrosion fatigue crack growth rate in Type 403 stainless steel in water. The results obtained by Speidel are shown in Figure 14. Figure 14 also shows the effect of frequency on the fatigue crack growth rate. Clark (69) conducted corrosion fatigue tests in air, distilled water,
Figure 14 Effect of frequency and heat treatment and environment on fatigue crack growth rate in Type 403 S.S. (Reference 68)
seawater, and sulfurous acid at 75°C and 200°C; he also tested in steam with high and low (40 ppm to < 1 ppm) oxygen content at 212°F. He found that the room temperature fatigue crack growth rates in Type 403 stainless steel were essentially identical in the above environments. However, at 200°F, the water, steam, and sulfurous acid environments increased the fatigue crack growth rate by factors of 2.5, 3, and 5, respectively, over that encountered in air. Logsdon (70) investigated the fatigue crack growth behavior of Type 403 stainless steel in distilled water at 520°F and 1200 psi pressure. He indicated that this environment had only a moderately adverse effect on the fatigue crack growth rate.

Abrego (71) studied the fatigue crack growth rate in Type 403 stainless steel in various environments such as air, distilled water, and sodium chloride, sodium sulfate, sodium phosphate and sodium silicate solutions. She found that, at open circuit potentials, the crack propagation rates were highest in distilled water, chloride and sulfate solutions. Corrosion fatigue was inhibited by high concentrations (1 M) of silicate or phosphate compounds. The effects of loading wave form and potential on corrosion fatigue crack growth rate were studied by Mack (72). He found that the crack growth rate in Type 403 stainless steel
in boiling distilled water was a function of loading wave form. Wave forms which have the same times from maximum to minimum load yielded the same fatigue crack growth rates. His results also showed that there was no effect of potential on the corrosion fatigue crack growth rates in Type 403 stainless steel in pH 12 sodium hydroxide solution at open circuit, passive or transpassive potentials. However, a significant effect on da/dN was seen in corrosion fatigue tests under applied cathodic potentials.

More recently, Ebara and his co-workers (73) studied the effect of heat treatment on the corrosion fatigue properties of 13% Cr stainless steel in 3% NaCl solution. Their results showed that the atmospheric fatigue strength was strongly affected by the tempering temperature but not by the austenizing temperature. They also found that fatigue crack growth rates in 3% NaCl solution were lower than those in air for AK's below 18 Mpa/√m, which is contrary to the results of Abrego (71).

2.5.2 Stress Corrosion Cracking in Type 403 Stainless Steel

A number of workers (6,68,74-77) have studied the SCC behavior of 12% Cr martensitic stainless steel as a function of heat treatment in various environments. Their results
showed that Type 403 stainless steel is susceptible to SCC in certain environments. Using fracture mechanics specimens, Speidel (68) found that the maximum stress corrosion crack growth rates were associated with the well-known 475 C embrittlement. As shown in Figure 15, SCC rates decrease with increasing tempering temperature from 25 C to 400 C, then increase to the maximum values at temperatures around 475 C. SCC rates again decrease to a low level with the tempering temperature above 500 C.

In relation to steam turbines, environmental contaminants that are of the greatest concerns are chloride, caustic, sulfide, and sulfate (78). It has been found that 12% Cr martensitic stainless steel is susceptible to SCC in sodium chloride (6,79-81), caustic (6,79), sulfide (6,78), and sulfate solutions. Using slow strain rate technique, Rao (79) found that there was no evidence of SCC in phosphate or silicate solutions.

A recent study on SCC of Type 403 stainless steel in 100 C sodium sulfate solution was performed by Bavarian and Szklarska-Smialowska (82). In a solution of pH 2, they found pitting occurred in the active/passive potential region. At pH 7 and 10, pitting occurred above a critical potential. Their results also indicated that SCC cracks
Figure 15  The effect of tempering temperature on stress corrosion cracking in 12% Cr steel. (Reference 68)
might nucleate intergranularly from corrosion pits, and then, propagate transgranularly depending on the pH, potential and temperature.

Bavarian, Moccari, and Macdonald (83) also studied the inhibition of SCC in Type 403 stainless steel in sodium sulfate solution. Using the slow strain rate test method, they found that sodium silicate was the only effective inorganic inhibitor for SCC of Type 403 stainless steel in sodium sulfate solution at 100 °C. However, there were several organic compounds which might act as SCC inhibitors for Type 403 stainless steel. These organic inhibitors, with the order of inhibiting efficiency on a molar concentration basis, are as follows:

octadecylamine > cyclohexylamine > hexylamine
> morpholine.

2.6 CORROSION FATIGUE AND STRESS CORROSION CRACKING IN INCONEL 600

2.6.1 Corrosion Fatigue in Inconel 600

Inconel 600 is the most widely used turbine material. Although the performance of this material in nuclear power generating plants has generally been good, there have been instances of cracking of this alloy. Most of the crackings
have generally been attributed to stress corrosion cracking. However, there have been incidents of cracking in Once Through Steam Generator (OTSG) in which the cracking events were attributed to fatigue (84-85). Fatigue failures of this turbine material are usually caused by flow-induced vibrations (85-86).

The stress corrosion cracking susceptibility of Inconel 600 has been studied extensively, however, only limited work has been done to characterize the fatigue and corrosion fatigue behavior of this material (39,87-88). Using round smooth specimens, Boateng et al (87) studied the fatigue behavior of Inconel 600 in air and in boiling caustic solution. They found that the hot concentrated caustic solution improved the fatigue life of Inconel 600. Sensitization, which is beneficial in hot caustic solution, was found to be detrimental in air. The results of their investigation are shown in Figure 16. In the fractographic examination they found that only the transgranular mode of fracture was observed in solution-annealed specimens, while the intergranular mode of cracking was observed for sensitized specimens fatigued both in air and in boiling caustic solution. Based on their results and the observations of Pessall (89) and Latanision et al (90), Boateng et al concluded that intergranular fracture occurs
because the grain boundary region is embrittled, but not because it is inherently more reactive in NaOH. Furthermore, they suggested that the beneficial effect of sensitization in NaOH solution may be attributed to the enrichment of Ni in the vicinity of the grain boundary.

Speidel (39) performed fatigue crack growth tests on solution-annealed and sensitized Inconel 600 specimens in air and molten NaOH at 335 C. The results are shown in Figure 17. He also found that SCC was intergranular, while the fatigue cracks in all environments studied at $10^{-3}$ to 10 Hz were transgranular. Therefore, he concluded that the stress corrosion crack velocity would not contribute significantly to the overall corrosion fatigue crack growth rate until the frequency of the load cycling dropped below $10^{-3}$ Hz.

The effect of cathodic potentials on the fatigue crack growth behavior of Inconel 600 has recently been studied by Was et al (88). They found that cathodic polarization of Inconel 600 during fatigue crack growth rate testing in 1 N $\text{H}_2\text{SO}_4$ resulted in an increased fatigue crack growth rate and a change in fracture mode under specific conditions. Based on their results they suggested that hydrogen embrittlement participates in the corrosion fatigue crack growth processes.
Figure 16 Stress-life curves of Inconel 600 in boiling 17.5 M NaOH solution. (Reference 87)
Figure 17  Effect of stress intensity amplitude and various environments on the growth rate of fatigue cracks in Inconel 600.  
(Reference 39)
at cathodic potentials, although the mechanism of hydrogen embrittlement in Inconel 600 is still not known.

2.6.2 Stress Corrosion Cracking in Inconel 600

It was reported in the early 1960's that Inconel 600 was liable to stress corrosion cracking (91-94). Since then, extensive efforts have been made to study the SCC phenomenon of Inconel 600 in various aqueous environments. There are many variables which are attributed to the occurrence of SCC in Inconel 600. In this review, however, we will limit our discussion to the effect of dissolved oxygen in solution, electrochemical potential and heat treatment on the SCC of Inconel 600.

2.6.2.1 Effect of Deaeration on SCC in Inconel 600

Dissolved oxygen in solution may affect the stress corrosion cracking behavior of Inconel 600 in the following ways: by altering the electrochemical potential, by producing different corrosion products or by changing the pH value of the solution. Van Booyen (95) pointed out that the corrosion potential of Inconel 600 in pure water may differ as much as 700 mV between aerated and deaerated conditions (based on the work of Syrett). The variation of the
electrochemical potential of Inconel 600 in pure water with the concentration of oxygen and hydrogen was reported by Park et al (96), and the result is presented in Figure 18. In general, the presence of oxygen in solution will increase the susceptibility of SCC of Inconel 600 in pure water (94,97-99). Copson and Dean (94) found that a large amount of oxygen plus a crevice did present a crack-prompting condition. Copson and Economy (97) investigated the effect of oxygen concentration on stress corrosion cracking of Ni-Cr-Fe alloys in pressurized water and found that intergranular attack increased with increasing oxygen concentration. Similar observations were reported by Clarke and Gordon (98) and Berry et al (99). However, intergranular SCC (IGSCC) of Inconel 600 was also reported in deaerated high purity (AVT) water (100).

The effect of oxygen in caustic solution on SCC of Inconel 600 is not well known. However, it has been found by Wilson et al (101) that high oxygen content was needed for SCC of Inconel 600 in caustic solution.

2.6.2.2 Effect of Potential on SCC in Inconel 600

The electrochemical potential of an alloy in aqueous environments may vary via the following ways: 1) galvanic
Figure 18 Open circuit potentials for Pt, Ni, Inconel 600, Type 304 S.S., and O₂ electrode as a function of H₂ and O₂ concentration in 0.1 m LiOH at 200 C. (Reference 96)
coupling, 2) changing the oxygen content in solution, or 3) controlling the specimen potential potentiostatically. The importance of the electrochemical potential on the SCC of material in aqueous solutions has been emphasized by Staehle (102) from the viewpoint of film stability. Van Rooyen (95) also indicated the potential dependence of SCC in Inconel 600. In the slow strain rate tests, Cels (103) reported that there is a threshold potential for Inconel 600 below which SCC will not occur in 10% NaOH solution at a temperature of 288 C. Cels (104) also found that a critical potential exists at which the cracks in Inconel 600 propagate most rapidly in deaerated 10% NaOH solution at 550 F. Theus (105) conducted controlled potential tests using spring-loaded specimens, and found that intergranular SCC in Inconel 600 occurred at potentials around 200mV with respect to the open circuit potential in 10% NaOH deaerated solution at 550 F. His results were in agreement with Cels' (104) results. Pessall et al (89) also studied the effect of the potential on the SCC behavior of Inconel 600 in 10% caustic soda solution at 315 C. They found that a maximum crack depth for highly stressed Inconel 600 specimen occurred in the potential range corresponding to the active-passive transition region of the anodic polarization curve.
The caustic stress corrosion cracking behavior of Inconel 600 at low temperatures (boiling NaOH solution) was studied at the Ohio State University (106-107). Park et al (106) found the crack propagation rate in Inconel 600 in boiling 17.5 M NaOH solution to be dependent on the potential. The maximum crack growth rate was calculated in the pseudo-passive region, and the minimum in the passive region. Most recently, Lee (107) studied the susceptibility of SCC of Inconel 600 in 25 M NaOH solution at 140°C under controlled potential conditions. He found that the most severe IGSCC in the mill annealed specimen occurred at potentials near either the anodic dissolution peak of Ni or the onset of the transpassive dissolution of Cr.

2.6.2.3 Effect of Heat Treatment on SCC in Inconel 600

Beneficial effect due to thermal treatment of Inconel 600 in aqueous media have been reported for SCC (95,104,108-114). In contrast to the SCC behavior of Type 304 stainless steel, in which sensitization results in a detrimental effect on SCC, the thermal treatment at temperatures around 700°C improves the SCC resistance of Inconel 600 in caustic solutions. As shown in the solubility diagram which is illustrated in Figure 19 (115), carbides are expected to precipitate at 700°C for most levels of
Figure 19 Solubility of carbon in Inconel 600. (Reference 115)
carbon content in Inconel 600. Several mechanisms (87,95,108) have already been proposed to explain this beneficial effect due to thermal treatment. It is generally believed that segregation of impurities, such as phosphorous (P), at the grain boundary will cause embrittlement. Van Booyen (95) proposed an incorporation mechanism in which the detrimental elements at the grain boundary are incorporated into the grain boundary carbides during heat treatment; the beneficial effect is consequently observed. Theus (108) proposed a mechanism which hypothesized the existence of an intermediate metallurgical condition between virgin mill-annealed material and fully stress relieved material that is detrimental to SCC resistance. The metallurgical condition is caused by diffusion processes which may enrich or deplete the grain boundary region with the detrimental elements. On the other hand, Boateng et al (87) argued that the improvement of SCC resistance of Inconel 600 by thermal treatment is due to the enrichment of Ni at the grain boundary region following loss of Cr to form carbides. This condition would decrease the corrosion rate in the vicinity of the grain boundary because the reactive element (Cr) is reduced, whereas Ni, which is principally responsible for corrosion resistance in NaOH solution, is increased. The reduced corrosion kinetics interacts with the crack
initiation process, the net effect being to delay initiation. Further work is required, however, to clearly examine the beneficial effect of thermal treatment on the SCC resistance of Inconel 600.

2.7 CORROSION FATIGUE AND STRESS CORROSION CRACKING IN TYPE 304 STAINLESS STEEL

Since Type 304 stainless steel has a wide range of engineering applications, the corrosion cracking problems of this material has been extensively studied in various aggressive environments. The first part of this section will deal with the corrosion fatigue studies and the next part will briefly mention the SCC studies.

2.7.1 Corrosion Fatigue in Type 304 Stainless Steel

Most of the corrosion fatigue studies on Type 304 stainless steel were conducted at near ambient temperatures. Using smooth round bar specimens, Boateng et al investigated the fatigue life of Type 304 stainless steel in boiling NaOH (116) and in H₂SO₄ (117). They found that the fatigue life of Type 304 stainless steel was drastically reduced due to the presence of either boiling NaOH or H₂SO₄. According to their results, anodic passivation is beneficial for static
loads in both solutions and small cyclic loads in $\text{H}_2\text{SO}_4$. However, the beneficial effect is eliminated by cyclic loading in boiling NaOH solution. Using fracture mechanics specimens, Miglin (118) studied the FCG rates in solution annealed Type 304 stainless steel in acid environments at room temperature. He found that the FCG rates and fracture morphology were dependent upon loading frequency. The experimental data also showed that in the passive region the action of the environment was retarded by film formation to the extent that the growth rates and fractographic results were comparable to those in air. The fatigue crack growth behavior of the as-received Type 304 stainless steel in boiling NaOH has also been studied. Boateng et al (87) found that boiling 17.5 M NaOH solution did not significantly accelerate crack growth rates in Type 304 stainless steel. They also found that the FCG rates were almost independent of potential, R ratio and frequency.

Recently, Ford and Silverman (36) and Ford and Emigh (119) studied the effect of loading rate on the fatigue crack growth rates in sensitized Type 304 stainless steel in high purity water at 95 C. Their data showed that the crack propagation rates are functions of the loading rate and the mean stress. In addition, they found that $K_{\text{isc}}$ will decrease with dynamic loading. Accordingly, $K_{\text{isc}}$ for
ductile/aqueous environment systems can not be regarded as a system constant.

Although extensive work has been done on the corrosion fatigue crack growth in Type 304 stainless steel in various aqueous environments near ambient temperatures, very limited work has been performed in high temperature BWR environments. Bamford (120) and Bamford and Moon (121) investigated the corrosion fatigue crack growth behavior of solution annealed austenitic stainless steel in BWR environments. They found that the environment had no effect on the FCG rate and that no frequency dependence of the crack growth rate existed at frequencies ranging from 0.17 Hz to 1 Hz. However, they found that the stress ratio had a significant effect on the crack growth behavior. Recently, a systematic study of corrosion fatigue crack growth behavior of Type 304 stainless steel in high temperature water was reported by Kawakubo et al (41). They investigated the fatigue behavior in oxygenated pure water at 290 C at various frequencies and loading wave forms. They found that the cracking mode of sensitized steel varied from transgranular to intergranular when the loading frequency was decreased. The corrosion fatigue crack growth behavior was also a function of the stress rise time, hence, it was dependent on the loading wave form. The effect of frequency
and wave form on the corrosion FCG rates as reported by Kawakubo et al (41) are shown in Figure 20.

The electrochemical potential may also have a significant influence on the corrosion fatigue crack growth behavior in BWR environments, however, no work was reported on this subject.

2.7.2 Stress Corrosion Cracking in Type 304 Stainless Steel

Stress corrosion cracking of austenitic stainless steel at low temperatures and at elevated temperatures has been thoroughly reviewed (122-123). The boundary defining the low temperature and the high temperature behavior is arbitrarily taken as 100 C by Cragnolino and Macdonald (122).

At low temperatures, the important role of the presence of oxygen in aqueous solutions on the intergranular stress corrosion cracking was reported (124-125). Ford and Povich (124) investigated the effect of different oxygen/temperature combinations on the stress corrosion susceptibility using the constant extension rate test (CERT). They found that SCC of sensitized Type 304 stainless steel can occur under dynamic loading conditions in water with oxygen/temperature combinations found under BWR startup.
Figure 20  Effect of loading frequency on time-based crack propagation rate of Type 304 S.S., tested in 290 C pure water with 8 ppm oxygen. (Reference 41)
operations. The susceptibility of IGSCC as a function of oxygen content and temperature was also reported by Ford and Silverman (125). Figure 21 shows a plot of oxygen/temperature combinations that are able to induce IGSCC.

Since the presence of oxygen in aqueous solution may change the corrosion potential of a material, the applied potential may have an effect on the SCC behavior of a material equivalent to that of the oxygen content. The potential dependence of the stress corrosion crack propagation rate of sensitized Type 304 stainless steel in 0.01 m Na$_2$SO$_4$ at 97°C has been studied. The results from the work of Ford et al (125) are presented in Figure 22. The crack growth rate was defined by the maximum crack penetration measured at the mid-thickness of a longitudinal section, divided by the test time. According to these results, rapid cracking is confined to a narrow potential range — in the neighborhood of +200 mV$_\text{NHE}$. 

At high temperatures, the SCC behavior of Type 304 stainless steel is quite different from that at low temperatures. Extensive work on the SCC of the austenitic stainless steel in BWR environments has been done by many investigators (126-134). The oxygen and potential dependence
Figure 21 Variation of stress corrosion susceptibility of sensitized Type 304 S.S. in BWR quality water for various oxygen/temperature combinations. (●) denotes no cracking; (x) denotes IGSCC cracking observed at an average propagation rate given by subscript number in cm S⁻¹ x 10⁻⁷, \( \dot{\epsilon} = 2.1 \times 10^{-7} \) S⁻¹. Hatched area denotes uncertainty of exact position of boundary line. (Reference 125)
Figure 22 Variation of average crack propagation rate of sensitized Type 304 S.S. in 0.01 m Na$_2$SO$_4$ at 97 ± 2 °C. (Reference 125)
of the SCC of sensitized Type 304 stainless steel has been recognized. The correlation between the dissolved oxygen concentration and the corrosion potential of Type 304 stainless steel in pure water at high temperature has been studied by Lee (135) and Indig and McIlree (131). The results of Indig et al (131) are shown in Figure 23. The corrosion potential increases with increasing concentration of dissolved oxygen. This indicates that at very low levels of oxygen content, the corrosion potential is controlled by the reduction of hydrogen ions, while at higher oxygen levels, this potential is controlled by the reduction of oxygen.

Using the slow strain rate test, Cragnolino et al (132) found that the SCC behavior of sensitized Type 304 stainless steel in 0.01 M Na₂SO₄ solution at 250°C is strongly dependent upon the applied potential. The results at various applied potentials in 0.01 M Na₂SO₄ solution at 250°C are shown in Figure 24. The variation of the ratio of time to failure in aqueous solution to that in argon at 250°C with potential is shown in Figure 25. These results indicate that a critical potential for IGSCC exists. In addition, a significant decrease in the elongation to failure occurs within the potential range of -400 to -200 mVₚᴴ.
Figure 23 The effect of dissolved oxygen concentration on the corrosion potential of Type 304 S.S. in high temperature purity water at 274 C. (Reference 131)
Figure 24  Nominal stress vs elongation curves for sensitized Type 304 S.S. in deaerated 0.01 m Na$_2$SO$_4$ at 250 C, at various potentials.  (Reference 132)
Figure 25  Ratio of elongation to failure in solution to that in argon as a function of potential and anodic polarization curve for sensitized Type 304 S.S. in 0.01 m Na₂SO₄ at 250 C.
(Reference 132)
The SCC behavior of Type 304 stainless steel can also be influenced by solution pH (136), degree of sensitization (137-140), carbon contents (141) and impurities (132), and cold work (142), etc. The effects of these variables on the SCC of Type 304 stainless steel have been thoroughly reviewed and discussed by Smialowska et al (123).
Chapter III
EXPERIMENTAL DETAILS

3.1 MATERIALS AND SPECIMEN GEOMETRY

Three kinds of materials, Type 403 stainless steel, Type 304 stainless steel, and Inconel 600, were used in this study. The major alloying elements of these materials are iron, chromium, and nickel. The compositions of Type 403 stainless steel, Type 304 stainless steel, and Inconel 600 are shown in Figure 26. Other alloying elements and impurities present in these materials are C, Mn, Mo, Co, Cu, Si, P, and S. Table 1 shows the mill chemistry of these alloys. The mechanical properties are presented in Table 2. Different heat treatments were applied to these materials. For Type 403 stainless steel, the materials were austenized at 950 C for 1 hour, cooled in air and then tempered at 650 C for 1 hour. For Type 304 stainless steel, the materials were first solution-annealed at 1050 C for 1 hour, water quenched, and then sensitized at 650 C for 10 hours. For Inconel 600, the materials were tested in the as-received
Figure 26 Compositions of Fe-Cr-Ni alloys used in this study.
<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Mn</th>
<th>I</th>
<th>S</th>
<th>Si</th>
<th>Mo</th>
<th>Cu</th>
<th>Co</th>
<th>N₂</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 403 S.S.</td>
<td>0.10</td>
<td>0.48</td>
<td>0.019</td>
<td>0.01</td>
<td>0.30</td>
<td>0.10</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>11.81</td>
<td>Bal.</td>
<td></td>
</tr>
<tr>
<td>Type 304 S.S.</td>
<td>0.13</td>
<td>1.13</td>
<td>0.030</td>
<td>0.022</td>
<td>0.40</td>
<td>0.47</td>
<td>0.74</td>
<td>0.13</td>
<td>0.056</td>
<td>8.06</td>
<td>18.38</td>
<td>Bal.</td>
</tr>
<tr>
<td>Inconel 600</td>
<td>0.070</td>
<td>0.22</td>
<td>--</td>
<td>0.003</td>
<td>0.10</td>
<td>--</td>
<td>0.27</td>
<td>--</td>
<td>--</td>
<td>75.8</td>
<td>15.2</td>
<td>8.32</td>
</tr>
</tbody>
</table>
### TABLE 2

**Mechanical Properties**

<table>
<thead>
<tr>
<th>Material</th>
<th>0.2 % Yield Strength</th>
<th>Ultimate Tensile Strength</th>
<th>% Elongation</th>
<th>% R.A.</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 403 S.S.(1)</td>
<td>85 Ksi (586 Mpa)</td>
<td>88 Ksi (607 Mpa)</td>
<td>25</td>
<td>67</td>
<td>22(Rc)</td>
</tr>
<tr>
<td>Type 304 S.S.(2)</td>
<td>38.5 Ksi (265 Mpa)</td>
<td>86.5 Ksi (596 Mpa)</td>
<td>57</td>
<td>76</td>
<td>156(BHN)</td>
</tr>
<tr>
<td>Inconel 600(2)</td>
<td>47.5 Ksi (327 Mpa)</td>
<td>107.5 Ksi (741 Mpa)</td>
<td>39</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

(1) After heat treatment,
(2) As-received condition.
condition. The heat treatments applied to these three different materials are summarized in Table 3. Microstructures of these materials are shown in Figures 27-29.

Compact tension (CT) specimens with 1.27 cm and 2.54 cm thickness were chosen to investigate the crack growth rates. Details of the specimen geometry are shown in Figure 30, and are in accordance with ASTM specification E399-72 (143). The specimens had a LT orientation, where the normal to the plane of the crack was parallel to the rolling direction and the crack propagation direction was parallel to the long transverse direction.

The K-calibration for this type of specimen in Model I is given by the expression (14):

\[ K_I = \frac{P}{BW\sqrt{a}} Y \quad (15) \]

where \( K_I \) = stress intensity factor in Model I.
- \( P \) = applied load,
- \( W \) = specimen width,
- \( B \) = thickness of specimen,
- \( a \) = crack length measured from load line,
- \( Y = 29.6 - 185.5(a/W) + 655.7(a/W)^2 - 1017(a/W)^3 + 638.9(a/W)^4 \)
<table>
<thead>
<tr>
<th>Material</th>
<th>Heat Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 403 S.S.</td>
<td>Austenized at 950 C (1750 F) for 1 hour, air cooled, tempered at 650 C (1200 F) for 1 hour.</td>
</tr>
<tr>
<td>Type 304 S.S.</td>
<td>Solution-Annealed at 1050 C for 1 hour, water quenched, then, sensitized at 650 C for 10 hours.</td>
</tr>
<tr>
<td>Inconel 600</td>
<td>As-received.</td>
</tr>
</tbody>
</table>
Figure 27 Microstructures of Type 403 S.S. : (a) As-received and x400, (b) quenched and tempered and x1000.
Figure 28 Microstructures of Inconel 600: (a) As-received and x530, (b) solution-annealed at 1120 C for 15 minutes followed by water quenching, and then thermally treated at 700 C for 1 hour followed by water quenching and x530.
Figure 29 Microstructures of Type 304 S.S.: (a) solution-annealed and x1000, (b) sensitized at 650 C for 10 hours and x1000.
Figure 30 Dimensions of half inch thick compact tension specimen.
Under cyclic loading, Equation 15 can be rewritten as follow:

\[ \Delta K = \Delta P / BW^{\alpha} \]
where \( \Delta K = K_{\text{max}} - K_{\text{min}} \)

= stress intensity factor range.

\( \Delta P = P_{\text{max}} - P_{\text{min}} \)

= applied load range.

3.2 TEST MATRIX

Since the environments where steam turbine blades, pipings and tubings are employed are not the same, the corrosion fatigue crack growth investigations described in this present work were performed in different solutions for different materials. In the study of the FCG behavior of Type 403 stainless steel the solutions investigated were 10 \( \text{m} \) \( \text{NaOH} \) and 6 \( \text{m} \) \( \text{NaCl} \) at 100 \( \text{C} \). The inhibitors used were sodium silicate (\( \text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O} \)) and sodium phosphate (\( \text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O} \)). In the study of corrosion fatigue in Inconel 600 and Type 304 stainless steel, the solutions employed were 0.01 \( \text{m} \) \( \text{H}_3\text{BO}_3 \) + 0.001 \( \text{m} \) \( \text{LiOH} \) and 0.01 \( \text{m} \) \( \text{Na}_2\text{SO}_4 \), respectively. The major variables which may have significant effects on the fatigue crack growth rates in the environments mentioned above are temperature, stress ratio \( (R) \), frequency \( (f) \) and
potential, etc. The test matrix for this study is shown in Table 4.

3.3 POLARIZATION STUDY

Polarization behaviors of Type 403 stainless steel in concentrated NaOH and NaCl solutions with and without the addition of inhibitors were studied. A cylindrical specimen with the dimensions of 0.6 cm diameter and 1.2 cm length was employed. The specimen was polished with 600 grit silicon carbide paper, then washed in distilled water and finally rinsed with acetone. It was subsequently mounted onto a stainless steel rod which was shielded with Teflon tubing, and put into a Teflon cell (Figure 31). The polarization study was conducted in a deaerated (argon purged) stagnant solution at 100 °C and at a potential scan rate of 20 mV/min, from the cathodic to the anodic direction. All measurements were referenced against a saturated calomel electrode (SCE).

The potentiodynamic polarization curve for sensitized Type 304 stainless steel in 0.01 M Na₂SO₄ solution at 250 °C was also determined using a potential sweep rate of 25 mV/min. The test was conducted in a recirculating autoclave system which will be described in the next section.
### TABLE 4

**Test Matrix**

<table>
<thead>
<tr>
<th>Variables</th>
<th>Materials</th>
<th>Environment</th>
<th>Inhibitor</th>
<th>Frequency (Hz)</th>
<th>Temperature (°C)</th>
<th>Potential</th>
<th>R</th>
<th>Wave Form</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type 403 S.S.</strong></td>
<td>Air</td>
<td></td>
<td>Na₂SiO₃</td>
<td>0.1</td>
<td>25</td>
<td>Open Circuit Potential</td>
<td>0.5</td>
<td>Sinusoidal</td>
</tr>
<tr>
<td></td>
<td>10 m NaOH</td>
<td></td>
<td>Na₃PO₄</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6 m NaCl</td>
<td></td>
<td></td>
<td>10</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Inconel 600</strong></td>
<td>Air</td>
<td></td>
<td></td>
<td>0.1</td>
<td>25</td>
<td>Open Circuit Potential</td>
<td>0.5</td>
<td>Sinusoidal</td>
</tr>
<tr>
<td></td>
<td>0.01 m H₃BO₃</td>
<td></td>
<td></td>
<td>1</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>+ 0.001 m LiOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Type 304 S.S.</strong></td>
<td>Air</td>
<td></td>
<td></td>
<td>0.008</td>
<td>25</td>
<td>Open Circuit Potential (-665 mV&lt;sub&gt;H&lt;/sub&gt;)</td>
<td>0.5</td>
<td>Sinusoidal</td>
</tr>
<tr>
<td></td>
<td>0.01 m Na₂SO₄</td>
<td></td>
<td></td>
<td>0.02</td>
<td>-450 mV&lt;sub&gt;H&lt;/sub&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.08</td>
<td>-200 mV&lt;sub&gt;H&lt;/sub&gt;</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
<td>+35 mV&lt;sub&gt;H&lt;/sub&gt;</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>+200 mV&lt;sub&gt;H&lt;/sub&gt;</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>
Figure 31  Schematic diagram of polarization testing cell.
3.4 APPARATUS AND PROCEDURES FOR CORROSION FATIGUE TESTS

3.4.1 Low Temperature Condition

3.4.1.1 Apparatus

Low temperature corrosion fatigue crack growth rate tests were performed on a 810 Material Test System (MTS) machine. It is a closed-loop servo-hydraulic system with a maximum load cell capacity of 100 Kips.

The aqueous solution was contained in a testing cell made of Teflon. The CT specimen in the cell is shown in Figure 32. The clevises, pins and pull rods were machined from Type 410 stainless steel. The dimensions of the holes and pins were machined in accordance with the ASTM specification to minimize the friction and to maintain in-plane rotation as the specimen is loaded (143). The testing cell was wrapped with a heating tape, and the solution was heated by this element. The temperature was controlled by means of a variac controller.

Crack length measurements were achieved using optical and compliance techniques. In open air tests, a 50X travelling microscope was used to measure the crack length.
Figure 32 Schematic drawing of low temperature corrosion fatigue testing cell.
on the specimen surface; and these measurements were accurate to within ± 0.001". The compliance technique was employed when the fatigue tests were conducted in aqueous environments. A linear variable differential transformer (LVDT) was used to continuously monitor the specimen compliance during the fatigue test. The arrangement of the LVDT is also illustrated in Figure 32. The LVDT and the core were supported, separately, by two mounting blocks which were made of Teflon and attached to the specimen on each side of the notch. The relative displacement of the LVDT and the core can be converted to the crack length, as will be discussed in the following section.

3.4.1.2 Procedure

Before the fatigue test, each specimen was precracked to about 2 mm. The purpose of precracking was to obtained a crack geometry as sharp as possible, in order to conform to the assumption made in $K_t$ analysis. Because a fatigue crack is considered to be the sharpest crack that can be reproduced in the laboratory, the machine notch is extended by fatigue. For the convenience of crack length measurement using a travelling microscope, an inverted haversine wave form was used to precrack the specimen. The precracking procedure suggested by Clark and Hudak (144) was followed.
This crack extension was accomplished in a series of steps starting at a high stress intensity and decreasing to a $\Delta K$ value which would be the initial value for subsequent corrosion fatigue testing. All precracking was done at a frequency of 10 Hz and an $R$ ratio of 0.1.

After precracking, the LVDT mounting blocks and holder were attached to the CT specimen. The specimen was then placed in the clevises and attached to the testing cell. The whole system was subsequently mounted to the MTS. The load cell, the testing cell and the actuator were perfectly aligned. Finally, the LVDT was positioned in its holder, and the testing solution was added to the testing cell. The solution was heated up to 100°C before the fatigue test started.

The fatigue test was performed using MTS in tension-tension load control mode with a sinusoidal wave form. The load was controlled by a MTS model 442.11 controller, and the error of the load was monitored by an oscilloscope and a MTS 430 digital indicator, being maintained within ±0.2%. The testing frequency and the load wave form were set by a MTS model 410.31 digital function generator; and the number of cycles was counted and displayed on a Model 417.01 counter panel. The crack opening displacement of the
specimen was monitored by the LVDT. The output signal of this LVDT was recorded using an Esterline-Angus recorder.

The corrosion fatigue test was continued until the LVDT output signal reached 3 V, which was equivalent to a crack length of 3.27 cm. Then, the load applied to the specimen was released, and the whole testing cell was unmounted from the MTS load frame. The fatigued CT specimen removed from the testing cell was subsequently pulled apart using MTS by applying a stress intensity greater than \( K_c \). The fractured surfaces were cut from the specimen and covered with acrylic spray coating to prevent any further oxidation before fractographic examination was performed. Finally, the fracture morphology was examined using scanning electron microscopy (SEM).

3.4.2 High Temperature and High Pressure Condition
3.4.2.1 Apparatus

High temperature and high pressure corrosion fatigue crack growth studies were performed using a Model 1331 20-Kip capacity electro-hydraulic Instron machine. This machine was arranged in parallel with the MTS, sharing the same power supply system. The functions which the Instron machine can perform are very similar to those of the MTS machine, although the operational procedures are different.
The testing chamber used for high temperature and high pressure corrosion fatigue tests was a one-liter autoclave fabricated from Inconel 600 alloy. Several ports were drilled through the top and the bottom of the autoclave to accommodate the pull rods, reference and counter electrodes, thermocouple, and solution inlet and outlet fittings. The pull rods and clevises were made of Inconel 600. Two pieces of spring-ring seals 1.90 cm in diameter were employed in the bottom pull rod to avoid leakage and to minimize friction. The specimen was electrically isolated from the rest of the system by a pair of pins machined from oxidized zirconium alloy (Zr + 2.5 Cb). A schematic diagram showing the autoclave and the CT specimen is presented in Figure 33. When controlled potential tests were conducted, the CT specimen was very carefully wrapped with Teflon Tape, so that only the loading pin holes and a strip of area (2 cm x 0.2 cm) ahead of the machine notch on both sides of the specimen were exposed to the solution. The potential of the specimen was measured and controlled using an external Ag/AgCl (in 0.1 M KCl) reference electrode (145), as shown in Figure 34. The potential was converted to the hydrogen scale using the data of Macdonald et al (145). A pair of platinum sheets were employed as counter electrodes. The relative positions of the CT specimen, reference electrode
Figure 33 Schematic diagram of high temperature and high pressure corrosion fatigue testing chamber.
Insulated support straps

PTFE
Ag/AgCl electrode

Cu tubing for air cooling

Type 316 reference compartment

PTFE

1/4" Al₂O₃ tube

PTFE tubing

Conax fitting

Figure 34  Ag/AgCl reference electrode assembly.
and counter electrodes in the autoclave assembly are shown in Figures 33 and 35. The autoclave cell incorporated with the Instron machine is shown in Figure 36.

The autoclave formed part of a recirculating loop (flow rate = 1 liter/hour) which permitted precise chemical and temperature control of the environment. The other components composing the recirculating system are described as follows.

A 20-liter stainless steel tank was used as a solution reservoir. The solution stored in this reservoir could be purged with any desired gas to establish and maintain chemical control. The autoclave and the reservoir were connected with tubes and heat exchangers. The solution was transferred and pressurized by a pulsating diaphragm pump. The autoclave was heated by an external heating tape, and the temperature of the solution inside the autoclave was measured by a J type thermocouple and controlled by a proportional temperature controller. The solution in the autoclave returns to the reservoir via a back pressure regulator.

A linear variable differential transformer was also used to continuously monitor the crack growth. Because of space limitations, and sealing and corrosion considerations, the LVDT core was mounted outside the autoclave on a movable
Figure 35 Relative positions of compact tension specimen, counter electrode and reference electrode.
Figure 36 View of assembly used to study the corrosion fatigue crack growth behavior in high temperature and high pressure aqueous environments.
pull rod, and the LVDT body was fixed on the stationary Instron machine platform. A calibration procedure was required to convert the LVDT output to the crack length.

3.4.2.2 Procedure

The CT specimen was installed into the autoclave after it was precracked (see Section 3.4.1.2) in MTS to 1-4 mm. The specimen was electrically isolated from the rest of the testing system by the use of a pair of pins fabricated from surface oxidized zirconium alloy, and it was connected to a Wenking ST 72 potentiostat with a piece of Teflon shielded Inconel 600 wire. Meanwhile, the reference and counter electrodes were placed in the proper positions. The load train (Instron load cell, pull rod, CT specimen, pull rod, and Instron actuator) was then perfectly aligned before the testing chamber was closed and sealed. The solution inlet and outlet fittings were also screwed onto the autoclave top and bottom, separately. The working, reference, and counter electrodes were then connected to the potentiostat; the cooling water was turned on to run through the cooling coils for the reference electrode and spring-ring seals; and the thermocouple was connected to the temperature controller.
The solution in the reservoir was purged with Ar gas to reach an oxygen content as low as 20 ppb, and then it was pressurized into the autoclave and heated to the desired test temperature.

After the solution pressure and temperature in the autoclave reached a steady state, the system was connected to the Instron actuator. The specimen inside the autoclave was then loaded to the mean level using the stroke-control mode. Since the tests were to be performed in tension-tension load-control mode, the Instron machine had to be transferred from stroke-control to load-control mode. This could be done by simply pressing the load mode transfer button in the Instron control panel.

The LVDT core was then connected to the pull rod and inserted into the LVDT body. Both the LVDT body and core were carefully positioned and aligned. Any misalignment of the LVDT could result in large errors in the measurement of the crack length. The LVDT output leads were connected to a Hewlett Packard digital voltmeter and an Esterline-Angus recorder. The recorder was in series with a timer which permitted the data to be recorded at a given time interval.

A load with a sinusoidal wave form and an R ratio of 0.5 was used for all the high temperature and high pressure
fatigue tests. Next the mean load was chosen, and then the load amplitude could be calculated and set on the load controller. After selecting the load waveform, setting the loading frequency and applying potential to the specimen, the corrosion fatigue test was started. The data generated during the fatigue test were number of loading cycles and LVDT voltage output, where the former was recorded in the Instron cycle counter and the latter was shown in the recorder. The test was usually started at a LVDT output voltage of 1.10 V and was terminated at 1.50 V, with corresponding crack lengths of about 2.3 and 3.2 cm, respectively. The load was then released and the heat and pressure being applied to the solution were removed before taking the CT specimen out of the testing chamber. Finally, the fatigued specimen was pulled apart using the MTS machine and the fracture surfaces were examined by SEM.

3.5 FATIGUE CRACK GROWTH RATE DATA REDUCTION

As indicated in Section 2.2.2, the fatigue crack growth rates in a given material depend on the range of variation of the stress intensity factor, $\Delta K$. In general, the fatigue crack growth results are presented as $\log(da/dN)$ versus $\log(\Delta K)$ curves, even in corrosive environments, where $da/dN$ is
the crack growth rate in meters/cycle (or inches/cycle) and \( \Delta K \) is the crack tip stress intensity factor range in \( \text{MPa}\sqrt{\text{m}} \) (or \( \text{ksi}\sqrt{\text{in}} \)). However, the raw data generated in a fatigue test are in the form of crack length, \( a \), which is measured optically, vs the number of elapsed cycles, \( N \). Therefore, complicated procedures are necessary to convert the raw data into the final form of the results. In the corrosion fatigue tests, the crack lengths are generally measured indirectly by either LVDT or potential drop, hence, the data reduction procedures are even more complicated. Since only the LVDT was employed, besides the travelling microscope, to monitor the crack length in this study, the following discussion is limited to these two techniques.

3.5.1 Conversion of Crack Length From Crack Opening Displacement

The linear variable differential transformer (LVDT) can be used to measure the crack opening displacement (COD) either in the gage line or in the load line. The crack length is then calculated from the crack opening displacement using the compliance technique. The relationship between the crack length and the compliance (\( \lambda \)) has been determined by Wilson et al (146). The compliance, \( \lambda \), is expressed as follows:

\[
\lambda = \frac{B\Delta S}{\Delta P}
\]  

(17)

where \( B \) is the thickness of the specimen,
\(E\) is Young's Modulus,
\(\Delta P\) is the cyclic load range, and
\(\Delta S\) is the difference between the maximum and the minimum load line crack opening displacements in a given loading cycle.

The relationship between \(a/W\) and load line \(\lambda\) for a CT specimen with \(H/W = 0.6\) is shown in Figure 37, where \(H\) is one half the value of the height of the specimen. The experimental data of the compliances obtained in this study are also shown in Figure 37. The load line compliance curve shown in Figure 37 can be expressed by the following equation:

\[
a/W = M_0 + M_1 \lambda + M_2 \lambda^2 + M_3 \lambda^3
\]

where \(M_0\), \(M_1\), \(M_2\), and \(M_3\) are regression coefficients. The coefficients resulting from curve fitting are as follows:

\[
M_0 = -0.21389362
M_1 = -1.68561652
M_2 = -0.10130821
M_3 = 0.41315835
\]

In the study of the corrosion fatigue behavior of Type 403 stainless steel, the gage line crack opening displacement, rather than the load line COD, was measured.
Figure 37 Compliance curves for compact tension specimen.
Therefore, the standard load line compliances should be converted to gage line values. This can be done simply by comparing the two similar triangles ABC and ADE in Figure 38. The resulting compliances are also shown in Figure 37. The gage line compliance curve can also be expressed by Equation 18 with the corresponding regression coefficients (M') shown as follows:

\[ M_0' = 0.261631 \]
\[ M_1' = -12.714346 \]
\[ M_2' = -0.033507 \]
\[ M_3' = 0.165344 \]

In the case of the high temperature and high pressure corrosion fatigue tests, the LVDT was arranged in such a way that the LVDT output included more than just the true load line crack opening displacement. The value of the true load line COD was determined as follows. The total difference in displacement, \( \Delta S \), measured using LVDT during a given loading cycle was:

\[ \Delta S = K_{cal} \times \Delta V \quad (19) \]

where \( K_{cal} = 0.01128 \) inches/Volt (LVDT calibration constant) and \( \Delta V \) = LVDT voltage output. The value of \( \Delta S \) can be divided into two parts, \( \Delta S \) and \( \Delta R \), where \( \Delta S \) is the true load line COD and \( \Delta R \) is contributed from the elastic elongation
\( a \) = crack length
\( x \) = distance from L.L. to G.L.
\( b = (BE \Delta \delta / \Delta P) \text{ LL} \)
\( y = (BE \Delta \delta / \Delta P) \text{ GL} \)

Triangles ABC and ADE are equiangular

\[
\frac{Y}{b} = \frac{a + x}{a}
\]

Figure 38 Conversion of standard load line compliance to gage line compliance for the compact tension specimen.
of the pull rods and the displacements of other parts of the load train. Therefore, the total displacement can be expressed as

\[ \Delta S = \Delta \delta + \Delta R \]  

(20)

Since the load control mode was used in this study, the second term on the right hand side of Equation 20 was assumed to be constant throughout a single test, and the value of \( \Delta R \) was then determined as follows. The average initial and final crack lengths were taken from five (or ten) measurements along the beach marks of the precrack front and the final crack front, as shown in Figure 39. The standard load line compliances for the initial crack length \( a_i \) and final crack length \( a_f \) could be obtained from Figure 37 or Equation 18. Then the corresponding standard values of \( \Delta \delta \) could be calculated from Equation 17. Using these results and the values of \( \Delta S \) recorded at the beginning and at the end of the test, \( \Delta R \)s can be calculated by Equation 20. It has been found that the values of \( \Delta R \) at the beginning and at the end of a test were almost the same. This result supported the assumption that the value of \( \Delta R \) was constant throughout any given test under load control mode. The average value of \( \Delta R \) at the beginning and at the end of the test was used as a calibration parameter to
Figure 39  Fatigue fracture surface of a compact tension specimen: (a) machine notch, (b) precrack, (c) corrosion fatigue crack, and (d) final failure where the specimen was pulled apart.
calculate the standard crack opening displacement difference, $\Delta S$.

After obtaining $\Delta S$, the actual crack length, $a$, could be calculated by Equations 17 and 18. One of the examples for the crack length measurement, with the LVDT core attached to the pull rod and in an open air system, is shown in Figure 40. The crack length measurement using the travelling microscope is also included in this figure for comparison. The results showed good agreement between these two methods and indicated that the indirect method for crack length measurement used in this study was reliable. Similar methods for fatigue crack length measurements have been reported and discussed elsewhere (147,148).

3.5.2 Fatigue Crack Growth Rate Determination

The crack tip stress intensity factor range is defined as: $\Delta K = K_{\text{max}} - K_{\text{min}}$, where $K_{\text{max}}$ and $K_{\text{min}}$ are the maximum and minimum values of the stress intensity factor at the crack tip. The stress intensity factor $K_t$ for a CT specimen is given in Equation 15. At constant applied load, the stress intensity factor range increases with the increasing crack length.
**Inconel 600**

Crack Length Measurement

- Visual (Travelling Microscope)
- Compliance (LVDT)

---

Figure 40 Fatigue crack length \( (a) \) as a function of loading cycles \( (N) \).
There are several methods for estimating the rate of fatigue crack growth. Among these are the graphical procedure, secant method, incremental polynomial method and total polynomial method. The incremental polynomial technique \((144,149)\) has gained increasing acceptance in recent years, and it is used in this study for data analysis. This method involves fitting successive sets of seven data points to a second order polynomial equation. The form of the equation is as follow:

\[
a = b_0 + b_1 \frac{(N - C_1)}{C_2} + b_2 \frac{(N - C_1)^2}{C_2}
\]  

(21)

where \(a\) is crack length, \(N\) is number of cycles, and \(b_i\) are regression parameters. The parameters \(C_1\) and \(C_2\) are used to scale the input data, thus avoiding numerical difficulties in determining the regression parameters \((144,149)\). For the case of a seven-point subgroup, \(C_1 = 1/2(N_{i-3} + N_{i+3})\), \(C_2 = 1/2(N_{i+3} - N_{i-3})\), and the local range of the crack length is \(a_{i-3} \leq a \leq a_{i+3}\) . The rate of crack growth at \((a_i, N_i)\) is obtained from the derivative of Equation 21, which is given by the following expression:

\[
\frac{da}{dN} = \frac{b_1}{C_2} + 2b_2 \frac{(N_i - C_1)}{C_2^2}
\]

(22)

The procedure mentioned above to convert the raw data \(a\) (or \(\Delta V\)) vs \(N\) to \(da/dN\) vs \(\Delta K\) is carried out by means of a
computer program. The final results are expressed as logarithms of the crack growth rate (log da/dN) vs logarithms of the stress intensity factor range (log ΔK). The steps of the data reduction procedure can be easily understood by examining the simplified schematic diagrams shown in Figure 41.
Figure 41 Schematic representation of data reduction steps with the compliance technique of crack growth measurement. (Reference 149)
Chapter IV

EXPERIMENTAL RESULTS AND DISCUSSION

4.1 EFFECT OF SILICATE AND PHOSPHATE ON THE FATIGUE CRACK GROWTH RATES IN TYPE 403 STAINLESS STEEL IN CONCENTRATED SODIUM CHLORIDE AND SODIUM HYDROXIDE SOLUTIONS

4.1.1 Electrochemical Studies

The corrosion parameters for the Type 403 stainless steel turbine blade alloy in deaerated 10 m NaOH and 6 m NaCl solutions containing various concentrations of Na$_2$SiO$_3$ and Na$_3$PO$_4$ (Table 5) are shown in Tables 6, 7, 8, and 9. All potentials are reported with reference to the saturated calomel electrode (SCE).

Polarization curves for Type 403 stainless steel in 10 m NaOH deaerated solution, with and without Na$_3$PO$_4$, are shown in Figure 42. Passive regions were observed in these systems. From Table 6 and Figure 42, we find only minor changes in the electrochemical behavior of Type 403 stainless steel in 10 m NaOH solution with the addition of Na$_3$PO$_4$ (pH=11). Polarization curves and corrosion

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### TABLE 5

Composition of Test Solution

<table>
<thead>
<tr>
<th></th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Saturated NaCl (6.6 m)</td>
</tr>
<tr>
<td>B</td>
<td>10 m NaOH</td>
</tr>
<tr>
<td>C</td>
<td>6 m NaCl + 0.1 m Na$_2$SiO$_3$</td>
</tr>
<tr>
<td>D</td>
<td>6 m NaCl + 0.5 m Na$_2$SiO$_3$</td>
</tr>
<tr>
<td>E</td>
<td>6 m NaCl + 0.1 m Na$_3$PO$_4$</td>
</tr>
<tr>
<td>F</td>
<td>6 m NaCl + 0.5 m Na$_3$PO$_4$</td>
</tr>
<tr>
<td>G</td>
<td>10 m NaOH + 0.1 m Na$_2$SiO$_3$</td>
</tr>
<tr>
<td>H</td>
<td>10 m NaOH + 0.5 m Na$_2$SiO$_3$</td>
</tr>
<tr>
<td>I</td>
<td>10 m NaOH + 0.1 m Na$_3$PO$_4$</td>
</tr>
<tr>
<td>J</td>
<td>10 m NaOH + 0.5 m Na$_3$PO$_4$</td>
</tr>
<tr>
<td>Solution</td>
<td>$E_{\text{corr.}}$ (mV)</td>
</tr>
<tr>
<td>--------------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>10 m NaOH</td>
<td>-1170</td>
</tr>
<tr>
<td>10 m NaOH + 0.1 m Na$_3$PO$_4$</td>
<td>-1160</td>
</tr>
<tr>
<td>10 m NaOH + 0.2 m Na$_3$PO$_4$</td>
<td>-1170</td>
</tr>
</tbody>
</table>

$E_{\text{corr.}}$: Corrosion Potential  
$E_{\text{cpp.}}$: Critical Potential for Passivation  
$i_{\text{cpp.}}$: Critical Current Density  
$i_p$: Passive Current Density  
$E_t$: Transpassive Potential
TABLE 7

Corrosion Parameters for Type 403 S.S. in 10 m NaOH + $x$ m Na$_3$SiO$_3$ Solution at 100 C.

<table>
<thead>
<tr>
<th>Solution</th>
<th>$E_{\text{corr.}}$ (mV)</th>
<th>$E_{\text{cpp.}}$ (mV)</th>
<th>$i_{\text{cpp.}}$ (mA/cm$^2$)</th>
<th>$i_{p}$ (mA/cm$^2$)</th>
<th>$E_{t}$ (mV)</th>
</tr>
</thead>
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<tr>
<td>10 m NaOH + 0.1 m Na$_2$SiO$_3$</td>
<td>-1160</td>
<td>-1080</td>
<td>$5.8 \times 10^{-1}$</td>
<td>$3.3 \times 10^{-2}$</td>
<td>-460</td>
</tr>
<tr>
<td>10 m NaOH + 0.2 m Na$_2$SiO$_3$</td>
<td>-1150</td>
<td>-1080</td>
<td>$5.4 \times 10^{-1}$</td>
<td>$1.9 \times 10^{-2}$</td>
<td>-460</td>
</tr>
</tbody>
</table>

See Table 6 for key.
TABLE 8

Corrosion Parameters for Type 403 S.S. in 6 m NaCl + x m Na$_2$SiO$_3$ Solution at 100 C.

<table>
<thead>
<tr>
<th>Solution</th>
<th>$E_{corr}$ (mV)</th>
<th>$E_{cpp}$ (mV)</th>
<th>$i_{cpp}$ (mA/cm$^2$)</th>
<th>$i_p$ (mA/cm$^2$)</th>
<th>$E_t$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated NaCl</td>
<td>-740</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>6 m NaCl + 0.005 m Na$_2$SiO$_3$</td>
<td>-925</td>
<td>-860</td>
<td>$4.7 \times 10^{-2}$</td>
<td>$2.3 \times 10^{-2}$</td>
<td>-250</td>
</tr>
<tr>
<td>6 m NaCl + 0.01 m Na$_2$SiO$_3$</td>
<td>-970</td>
<td>-890</td>
<td>$4.7 \times 10^{-2}$</td>
<td>$2.0 \times 10^{-2}$</td>
<td>-270</td>
</tr>
<tr>
<td>6 m NaCl + 0.05 m Na$_2$SiO$_3$</td>
<td>-1029</td>
<td>-950</td>
<td>$5.8 \times 10^{-2}$</td>
<td>$1.5 \times 10^{-2}$</td>
<td>+38</td>
</tr>
<tr>
<td>6 m NaCl + 0.1 m Na$_2$SiO$_3$</td>
<td>-1040</td>
<td>-1000</td>
<td>$5.6 \times 10^{-2}$</td>
<td>$1.7 \times 10^{-2}$</td>
<td>+140</td>
</tr>
<tr>
<td>6 m NaCl + 0.2 m Na$_2$SiO$_3$</td>
<td>-1060</td>
<td>-980</td>
<td>$4.8 \times 10^{-2}$</td>
<td>$1.8 \times 10^{-2}$</td>
<td>+126</td>
</tr>
</tbody>
</table>

See Table 6 for key.
TABLE 9
Corrosion Parameters for Type 403 S.S. in 6 m NaCl + xm Na$_3$PO$_4$ Solution at 100 C.

<table>
<thead>
<tr>
<th>Solution</th>
<th>$E_{corr.}$ (mV)</th>
<th>$E_{cpp.}$ (mV)</th>
<th>$i_{cpp.}$ (mA/cm$^2$)</th>
<th>$i_p$ (mA/cm$^2$)</th>
<th>$E_t$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 m NaCl + 0.01 m Na$_3$PO$_4$</td>
<td>-948</td>
<td>-850</td>
<td>$4.3 \times 10^{-2}$</td>
<td>$2.5 \times 10^{-2}$</td>
<td>-310</td>
</tr>
<tr>
<td>6 m NaCl + 0.05 m Na$_3$PO$_4$</td>
<td>-976</td>
<td>-900</td>
<td>$3.9 \times 10^{-2}$</td>
<td>$2.2 \times 10^{-2}$</td>
<td>-210</td>
</tr>
<tr>
<td>6 m NaCl + 0.1 m Na$_3$PO$_4$</td>
<td>-995</td>
<td>-900</td>
<td>$3.7 \times 10^{-2}$</td>
<td>$2.2 \times 10^{-2}$</td>
<td>0</td>
</tr>
<tr>
<td>6 m NaCl + 0.25 m Na$_3$PO$_4$</td>
<td>-1025</td>
<td>-920</td>
<td>$2.9 \times 10^{-2}$</td>
<td>$1.2 \times 10^{-2}$</td>
<td>+190</td>
</tr>
<tr>
<td>6 m NaCl + 0.3 m Na$_3$PO$_4$</td>
<td>-1015</td>
<td>-920</td>
<td>$2.9 \times 10^{-2}$</td>
<td>$1.5 \times 10^{-2}$</td>
<td>+130</td>
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<td>6 m NaCl + 0.4 m Na$_3$PO$_4$</td>
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<td>-920</td>
<td>$4.0 \times 10^{-2}$</td>
<td>$2.0 \times 10^{-2}$</td>
<td>+190</td>
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<tr>
<td>6 m NaCl + 0.5 m Na$_3$PO$_4$</td>
<td>-1025</td>
<td>-920</td>
<td>$3.4 \times 10^{-2}$</td>
<td>$1.8 \times 10^{-2}$</td>
<td>+180</td>
</tr>
</tbody>
</table>

See Table 6 for key.
parameters for Type 403 stainless steel in 10 m NaOH with the addition of Na$_2$SiO$_3$ (pH=11) are shown in Figure 43 and Table 7. The curves differ slightly from the curves in pure 10 m NaOH solution as shown in Figure 42. However, increasing the concentration of Na$_2$SiO$_3$ from 0.1 m to 0.2 m resulted in a decrease in the passive current density ($3.4 \times 10^{-2}$ mA/cm$^2$ to $1.0 \times 10^{-2}$ mA/cm$^2$). Tables 8 and 9 list the major corrosion parameters for Type 403 stainless steel in 6 m NaCl solution with the addition of the inhibitors. In the deaerated saturated sodium chloride solution (pH=11), the corrosion potential is -740 mV$_{SSC}$, which is about 260 mV more negative than that obtained in the solution exposed to air. The polarization curves for Type 403 stainless steel tested both in the solution exposed to air and the solution which was flushed with argon are shown in Figure 44. Passive behavior was not observed in these environments.

It can be seen from Table 8 and Figure 45 that the addition of sodium silicate to 6 m sodium chloride solution (pH=11) changes the corrosion behavior dramatically. The corrosion potential was shifted in the cathodic direction with the addition of sodium silicate, and passive behavior was observed, with the passive current density on the order of about $2 \times 10^{-2}$ mA/cm$^2$. Furthermore, the corrosion potential was shifted more in the cathodic direction, and
the passive region was expanded with increasing concentrations of sodium silicate. The changes in the corrosion potential and the transpassive potential of Type 403 stainless steel depending on the concentration of sodium silicate in 6 m sodium chloride solution are shown in Figures 46 and 47. The changes are primarily due to the increase of the pH value.

Table 9 shows the corrosion parameters of Type 403 stainless steel in 6 m sodium chloride solutions which were inhibited by sodium phosphate (pH=11). The results are very similar to those in the 6 m NaCl + x m Na₂SiO₃ solutions, as shown in Figure 48. In the deaerated solutions, sodium phosphate shifts the corrosion potential in the cathodic direction, delays transpassive corrosion, and expands the passive range. The changes in the corrosion potential and transpassive potential with increasing concentration of sodium phosphate in 6 m sodium chloride solution at 100 °C are shown in Figures 49 and 50, respectively. Again, the increase of the pH is responsible for the change in the electrochemical behavior. As demonstrated by other researchers (150-153), the inhibitory action of sodium silicate and sodium phosphate is more effective in the presence of oxygen. The effect of these compounds in sodium chloride solution are shown in Figures 51 and 52,
Figure 42 Effect of sodium phosphate concentration on the potentiodynamic polarization of Type 403 S.S. in deaerated 10 m sodium hydroxide solution at 100 °C.
Figure 43 Effect of sodium silicate concentration on the potentiodynamic polarization of Type 403 S.S. in deaerated 10 m sodium hydroxide solution at 100 C.
Figure 44  Potentiodynamic polarization of Type 403 S.S. in air-exposed and deaerated saturated sodium chloride solution at 100 C.
Figure 45  Effect of sodium silicate concentration on the potentiodynamic polarization of Type 403 S.S. in deaerated 6 m sodium chloride solution at 100 C.
Figure 46 Effect of sodium silicate concentration on the corrosion potential of Type 403 S.S. in deaerated 6 m sodium chloride solution at 100 C.
Figure 47 Effect of sodium silicate concentration on the transpassive potential of Type 403 S.S. in deaerated 6 m sodium chloride solution at 100 C.
Figure 48 Effect of sodium phosphate concentration on the potentiodynamic polarization of Type 403 S.S. in deaerated 6 m sodium chloride solution at 100°C.
Figure 49 Effect of sodium phosphate concentration on the corrosion potential of Type 403 S.S. in deaerated 6 m sodium chloride solution at 100 C.
Figure 50  Effect of sodium phosphate concentration on the transpassive potential of Type 403 S.S. in deaerated 6 m sodium chloride solution at 100 C.
Figure 51 Effect of sodium silicate concentration on the potentiodynamic polarization of Type 403 S.S. in air-exposed 6 m sodium chloride solution at 100 C.
Figure 52 Effect of sodium phosphate concentration on the potentiodynamic polarization of Type 403 S.S. in air-exposed 6 m sodium chloride solution at 100 C.
respectively. The presence of oxygen in the solution participates in the cathodic reaction and shifts the potential in a more positive direction. Also, the corrosion current decreases about one order of magnitude, and the anodic current density is much less than that obtained in deaerated solutions.

From the above results, it appears that sodium silicate and sodium phosphate have similar inhibition characteristics.

4.1.2 Corrosion Fatigue Studies—Behavior in Absence of Inhibitors

The fatigue crack growth rates at a frequency of 10 Hz and \( R = 0.5 \) in air at room temperature, and in saturated sodium chloride and in 10 m sodium hydroxide solutions at 100°C are summarized in Figure 53. This figure shows that the concentrated sodium chloride solution was the most aggressive environment studied for crack propagation in Type 403 stainless steel.

The effect of test frequency on the FCG rates in 10 m NaOH solution at 100°C is shown in Figure 54. Decreasing the frequency from 10 Hz to 1.0 Hz gave rise to higher fatigue crack growth rates. The fractographs of specimens tested in
10 m sodium hydroxide solution at 10 Hz and 1.0 Hz are shown in Figure 55. The fractured surfaces exhibit both transgranular and intergranular fracture modes.

Figure 56 shows the effect of test frequency on the FCGR rates in Type 403 stainless steel in sodium chloride solution at 100 C. As expected, crack growth rate increased with decreasing the frequency from 10 to 1 Hz. However, the changes in crack growth rate at frequencies between 0.1 and 1.0 Hz were relatively small, and they were almost the same at high ΔK values. Figure 57 shows the fractographic results of specimens tested in saturated sodium chloride solution. In the 10 Hz test, only transgranular fractures were observed. However, at 1.0 Hz and 0.1 Hz, mixed intergranular and transgranular fractures were found. The intergranular fractures became more pronounced at lower frequencies.

4.1.3 Corrosion Fatigue Studies—Behavior in Presence of Inhibitors

The effect of 0.1 m sodium phosphate and 0.1 m sodium silicate upon corrosion fatigue crack growth rates in 10 m sodium hydroxide solution at 100 C are depicted in Figure 58. The results showed that both 0.1 m sodium phosphate and 0.1 m sodium silicate did not affect the FCGR rates in this
Figure 53 Fatigue crack growth rate in Type 403 S.S. in air, 10 m NaOH and saturated NaCl at open circuit potential and at a frequency of 10 Hz.
Figure 54  Effect of frequency on the fatigue crack growth rate in Type 403 S.S. in 10 m NaOH at 100 C and open circuit potential.
Figure 55 SEM of corrosion fatigue fracture surfaces of Type 403 S.S. in 10 m sodium hydroxide solution: (a) 1.0 Hz and x500, (b) 10 Hz and x500.
Figure 56 Effect of frequency on the fatigue crack growth rate in Type 433 S.S. in saturated sodium chloride solution at 100°C and open circuit potential.
Figure 57  SEM of corrosion fatigue fracture surfaces of Type 403 S.S. in saturated sodium chloride solution: (a) 0.1 Hz and x500, (b) 1.0 Hz and x500, and (c) 10 Hz and x1000.
Increasing the concentration of both compounds to 0.5 m still had no effect on the crack growth rate, as shown in Figure 59. These results do, however, confirm those observed in the electrochemical studies. Figure 60 shows SEM micrographs of the surfaces of samples fatigued at 1.0 Hz in 10 m sodium hydroxide solution containing 0.1 and 0.5 m sodium phosphate and sodium silicate. These surfaces were covered with a non-uniform corrosion product film which was rather thick when both compounds were at a concentration of 0.5 m. After removing the surface corrosion product film (by 50% HCl + 2 gs/l of hexamethylenetramine), the fracture surfaces were examined again and the results are shown in Figure 61. The fracture surfaces were still in transgranular/intergranular modes; the additives did not change that pattern significantly.

The effect of sodium phosphate and sodium silicate on the fatigue crack growth rates in Type 403 stainless steel in 6 m sodium chloride solution at 100 C is shown in Figures 62 and 63. These figures reveal that both additives had the same effect on the FCG rates in 6 m sodium chloride. Figure 62 shows that the addition of 0.1 m Na₃PO₄ or Na₂SiO₃ caused a slight increase in the FCG rates at a frequency of 1 Hz, but that the addition of 0.5 m decreased the FCG rates to the level observed in air, as shown in Figure 63. SEM
Figure 58  Effect of 0.1 sodium phosphate and 0.1 m sodium silicate on the fatigue crack growth rate in Type 403 S.S. in 10 m sodium hydroxide solution at 100°C, open circuit potential and 1.0 Hz.
Figure 59  Effect of 0.5 m sodium phosphate and 0.5 m sodium silicate on the fatigue crack growth rate in Type 403 S.S. in 10 m sodium hydroxide solution at 100 C, open circuit potential and 1.0 Hz.
Figure 60  Corrosion fatigue fracture surfaces (covered by corrosion product) of Type 403 S.S. at a frequency of 1 Hz. (a) 10 m NaOH + 0.1 m \( \text{Na}_3\text{PO}_4 \) and x3000, (b) 10 m NaOH + 0.1 m \( \text{Na}_2\text{SiO}_3 \) and x3000, (c) 10 m NaOH + 0.5 m \( \text{Na}_3\text{PO}_4 \) and x1000, and (d) 10 m NaOH + 0.5 m \( \text{Na}_2\text{SiO}_3 \) and x1000.
Figure 61  Corrosion fatigue fracture surfaces, after corrosion product being removed, of Type 403 S.S. at a frequency of 1 Hz. (a) 10 m NaOH + 0.1 m Na$_3$PO$_4$ and x500, (b) 10 m NaOH + 0.1 m Na$_2$SiO$_3$ and x500, (c) 10 m NaOH + 0.5 m Na$_3$PO$_4$ and x500, and (d) 10 m NaOH + 0.5 m Na$_2$SiO$_3$ and x500.
micrographs of specimens tested in 6 m sodium chloride solution in the presence of the additives are shown in Figure 64. At 1.0 Hz frequency and with the presence of 0.1 molal additive, the fractured surface exhibited an intergranular failure mode. At 10 Hz frequency and with the presence of 0.5 molal additive, the fracture surfaces revealed only transgranular cracking. This failure mode is similar to that observed in pure saturated chloride solution, even though the fatigue crack growth rates determined in pure chloride solution were higher (by an order of magnitude) than those obtained in the inhibited solutions.

4.1.4 Discussion

4.1.4.1 Effect of Environment and Frequency on The Corrosion Fatigue Behavior in The Absence of Additives

The results found in this study show that chloride solution is more aggressive than sodium hydroxide solution in promoting the corrosion fatigue crack growth behavior of Type 403 stainless steel. These results are in agreement with the findings of Abrego (71), who found that the fatigue crack growth rates in this material are almost the same in pure water, chloride solutions and sulfate solutions and are
Figure 62 Effect of 0.1 m sodium phosphate and 0.1 m sodium silicate on the fatigue crack growth rate in Type 403 S.S. in 6 m sodium chloride at 100 C, open circuit potential and 1.0 Hz.
Figure 63 Effect of 0.5 m sodium phosphate and 0.5 m sodium silicate on the fatigue crack growth rate in Type 403 S.S. in 6 m sodium chloride at 100 C, open circuit potential and 10 Hz.
Figure 64  Fatigue fracture surfaces of Type 403 S.S. (a)  
6 m NaCl + 0.1 m Na$_3$PO$_4$, 1.0 Hz and x1000, (b)  
6 m NaCl + 0.1 m Na$_2$SiO$_3$, 1.0 Hz and x1000, (c)  
6 m NaCl + 0.5 m Na$_3$PO$_4$, 10 Hz and x1000, and  
(d) 6 m NaCl + 0.5 m Na$_2$SiO$_3$, 10 Hz and x1000.
higher than in sodium silicate and sodium phosphate solutions (which exhibit higher pH). She also noted that the values of da/dN are approximately the same regardless of the chloride ion concentration (0.1 to 1.0 M).

Fatigue crack growth rates in this material in sodium hydroxide solution are higher than those in air environment, however, they are about two times lower than those found in chloride solution. For specimens tested in sodium hydroxide solution, a black, thick and relatively adherent film of corrosion products covered the surfaces of the specimens. On the other hand, no discernable corrosion product was observed on the surfaces of the specimens tested in sodium chloride solution. Therefore, the lower FCG rate in sodium hydroxide solution could be due to the presence of the surface film. It is obvious that anions are primarily responsible for the difference in the corrosion fatigue crack growth behaviors.

In sodium hydroxide solution, the environmental acceleration of the FCG rates increased with decreasing frequency. The fatigue crack growth rates were about two times higher when the loading frequency was decreased from 10 Hz to 1 Hz. At the lower frequencies, the time for the reaction between the material and the corrosive environment
is longer; therefore, the contribution to the crack propagation due to the environment is higher for a given loading cycle.

Although the FCG rates were independent of the chloride ion concentration, they changed with loading frequency. As expected, crack growth rate increases when frequency decreases from 10 to 1 Hz. However, the changes in crack growth rates between 0.1 and 1.0 Hz frequencies were relatively small, and they are almost the same at high $\Delta K$ values. The FCG rates (per cycle) increase with decreasing loading frequency in most material/environment systems. In general, this enhancement is believed to be due to the SCC effect as indicated in Equation 12. However, this is not the case for the Type 403 stainless steel/sodium chloride solution system. The results found in this study show that the value of $da/dN$ reached a maximum or saturation value at low frequencies. The reasons for this kind of behavior are not known. However, one tentative explanation for this observation is that the fatigue crack growth in this system is limited by the reaction between the material and the environment.
4.1.4.2 Effect of Additives on The Fatigue Crack Growth Behavior

The presence of silicate or phosphate in sodium hydroxide solutions did not affect the corrosion fatigue behavior of Type 403 stainless steel. The fatigue crack growth rates determined were in agreement with the results observed in the electrochemical studies. It was mentioned previously that the presence of hydroxyl ions in water results in the decrease of the fatigue crack growth rate. Ogura (154) found that hydroxyl ions play an important role in the passivation of iron. From the point of view of inhibition, the hydroxyl ion is in essence an inhibitor for the corrosion fatigue behavior of Type 403 stainless steel. Since the material could be easily passivated in hydroxide solution, the addition of passivating anions (silicate or phosphate) would have only a minor effect. Therefore, the FCG rates in hydroxide solution would not be affected by the presence of these inorganic compounds. However, EDAX examinations showed the presence of P and Si on the fractured surfaces. This implies that these compounds were incorporated into the growing corrosion product films, or at least were extensively adsorbed onto the surfaces.

The presence of chloride ions in distilled water might result in a localized acidification of the crack tip. This
would lead to a higher dissolution rate, thereby resulting in a high crack growth rate. If an insufficient amount of inhibitor was present in the system, incomplete surface coverage, particularly on the cathodic surfaces, would result in the formation of larger and more efficient cathodic areas coupled to smaller anodic areas (155). This unfavorable cathode to anode ratio would promote rapid selective attack at the local anode at the crack tip. This mechanism might account for the slight increase in fatigue crack growth rates in Type 403 stainless steel when 0.1 molal of silicate or phosphate was added to 6 molal chloride solution, as shown in Figure 62. However, the reduction in the FCG rates upon addition of 0.5 m of the inhibitors was almost by an order of magnitude, such that no environmental acceleration of the FCG of Type 403 stainless steel occurred. The effect of the additives in these cases was very similar to that observed with high-strength aluminum alloys in chloride solutions (156).

Stoltz and Pelloux (157) studied the inhibition of corrosion fatigue of 7075 aluminum alloy in chloride solution using sodium nitrate as an inhibitor. They found that when sufficient quantities of sodium nitrate were added to distilled water and to aqueous sodium chloride solutions, the fatigue crack growth rates were reduced to those
observed in dry air. This reduction in fatigue crack growth rate was explained by a surface site competition mechanism between $\text{Cl}^-$ and $\text{NO}_3^-$ ions. The reduction in corrosion fatigue crack growth in this present study, however, could be attributed to the formation of insoluble compounds such as iron phosphate or iron silicate on the metal surface, which would promote passivity (158). Furthermore, the addition of phosphate or silicate could result in an increase of the pH of the solution, and hence could cause the increase in passivation (151).
4.2 Corrosion Fatigue Crack Growth in Inconel 600 in Simulated Pure Environments

4.2.1 Corrosion Fatigue Crack Growth Rates

In the present study, the corrosion fatigue crack growth tests were only conducted on the as-received Inconel 600 alloy. The obtained corrosion fatigue crack growth results are summarized in Figures 65 to 69.

Fatigue crack growth rates in Inconel 600 (as-received) were studied in air at room temperature (25°C) and at a frequency of 10 Hz. Both optical measurement and compliance techniques were used to measure the crack lengths (see Figure 40). The growth rates determined by these two methods are shown in Figure 65. The fatigue crack growth rates in Inconel 600 in air which were duplicated using the MTS machine are also shown in Figure 65 for comparison. It can be seen that the results determined by the optical method and the compliance method are in agreement; they are therefore used as a basis for further comparisons.

The fatigue crack growth rates in Inconel 600 in air at 25°C and a frequency of 1 Hz were also tested in the autoclave testing chamber. The results of this experiment are shown in Figure 66. A small discrepancy between the results obtained in open air and those obtained in the
an autoclave was found. The difference could be due to misalignment of the pull rods and the LVDT. However, the disagreement was so small as to be unimportant. More discussion on the crack length measurement will be presented in Section 4.2.3. The second specimen tested in the autoclave was fatigued in air at 200 °C and a frequency of 1 Hz. As shown in Figure 67, the fatigue crack growth rates at 200 °C were the same as those determined at room temperature.

Corrosion fatigue tests were conducted in 0.01 m H$_3$BO$_3$ + 0.001 m LiOH solution at temperatures ranging from 100 °C to 250 °C. The solutions were air-saturated except the one tested at 100 °C. The fatigue crack growth rates generated in these simulated PWR primary environments are shown in Figure 68. These results indicate that the solution studied exerts no environmental effect on the fatigue crack growth rates in as-received Inconel 600.

The effect of frequency on the fatigue crack growth rates at 200 °C is shown in Figure 69. The results demonstrate that there is no frequency effect on the fatigue crack growth rate in 0.01 m H$_3$BO$_3$ + 0.001 m LiOH solution at frequencies above 0.1 Hz.
Figure 65  Fatigue crack growth rates in Inconel 600, tested in air at 25°C, 10 Hz.
Figure 66  Fatigue crack growth rates in Inconel 600 in air, tested in autoclave at 25 °C, 1 Hz.
Figure 67  Fatigue crack growth rates in Inconel 600 in air, tested in autoclave at 200 °C, 1 Hz.
Figure 68  Fatigue crack growth rates in Inconel 600, tested in 0.01 m \( \text{H}_2 \text{BO}_3 \) + 0.001 m LiOH solution at 100°C, 130°C, 200°C, and 250°C, 1 Hz.
Figure 69  Effect of frequency on the fatigue crack growth rates in Inconel 600 in 0.01 m $H_3BO_3 + 0.001 m$ LiOH at 200 C.
4.2.2 **Practographic Results**

Fracture surfaces of every CT specimen were examined by SEM after fatigue cracking. In spite of the difference of environments (air or 0.01 m $\text{H}_3\text{BO}_3 + 0.001$ m LiOH solution), temperatures and frequencies, the fracture modes were all clearly transgranular. An example of the fracture morphology of Inconel 600 fatigued in 0.01 m $\text{H}_3\text{BO}_3 + 0.001$ m LiOH solution at 200°C and a frequency of 0.1 Hz is shown in Figure 70. No intergranular facets were found on the fractured surfaces.

4.2.3 **Discussion**

4.2.3.1 **Uncertainty in The Crack Length Measurement**

The reliability of the determined fatigue crack growth rates determined depends on the variability inherent in both the data collection and data processing techniques. The latter was fully discussed by Clark and Hudak (152) and will not be presented in this study. The accuracy of the measurement of crack length in high temperature and high pressure environments, however, was of major concern to the author.
Figure 70  Fracture surface of Inconel 600 after fatigue cracking in 0.01 m H$_3$BO$_3$ + 0.001 m LiOH solution at 200 C and 0.1 Hz.
In general, crack length measurement during the fatigue tests is performed by one of the following methods: optical measurement using a travelling microscope, the potential drop (AC or DC) method (36,159), the compliance technique using the LVDT etc. Only the LVDT was employed in this study because of the shortcomings of the other methods. For example, the optical method cannot be used in corrosion fatigue tests because the specimen is enclosed in a container. In an environment where the electrochemical potential is a controlled variable, the use of the potential drop technique is not appropriate. One other method which has been used is the direct measurement of the crack length on both sides of a specimen removed from the testing cell after cyclic testing (41). This process is repeated several times on the same specimen and the crack growth rate is calculated from the average crack length and the number of loading cycles in each step. The disadvantages of this discontinuous process are the long period of time involved and the possible change of the environment at each step.

Based on the above considerations, the compliance method using the LVDT was employed in this study. The LVDT may be arranged in the way either described in Section 3.4.1.1 or in Section 3.4.2.1. In high temperature and high pressure conditions, the arrangement as described in Section
3.4.1.1 involved considerable difficulty with the sealing of the autoclave system, a major concern of the operation. It was also possible to install the LVDT inside the autoclave, but corrosion problems with the LVDT would be encountered. Therefore, the LVDT was installed outside the autoclave in such a way that a correction factor could be included in order to obtain the true crack opening displacement. As one might expect, a greater uncertainty will thus be introduced, and this will be briefly discussed below.

The value of $\Delta R$ in Equation 20 is much greater than the value of $\Delta\delta$. A small variation of $\Delta R$ may result in a great change in the crack length measurement. Therefore, the determination of $\Delta R$ is very important to the data reduction process. The precision of the raw data and $\Delta R$ measurement depends on the stability of the measuring device. It is vital to install the LVDT core and body in stable positions and to have them be well aligned. The prevention of interference from the surroundings during the test is important as well. Despite the cautious procedures followed, the LVDT outputs were not consistent in some cases and a great deal of scatter in the raw data might have occurred. The inconsistency might be due to thermal and/or pressure fluctuations, or to friction between the pull rod and fitting, etc. When a great amount of scatter was
encountered, the data were usually not used. But in most cases the scatter was so small that average values were taken. As a matter of fact, the results obtained in the tests performed in high temperature and high pressure conditions (Section 4.2 and 4.3) involved greater uncertainties than those obtained in low temperature tests (Section 4.1). However, it was found that the uncertainty in the crack length measurement was usually within ±20 mils, which corresponds to about 1 Mpa√m variation in the stress intensity factor range with ΔK in the range of 15-25 Mpa√m. This error was so small as to be insignificant. Although small discrepancies were noted in Figures 40, 65, and 66, the results in these figures clearly indicated that the method employed in this study was quite acceptable. Moreover, since it is the trend of the corrosion fatigue crack growth behavior which is most important for our understanding of the cracking phenomenon in high temperature aqueous environments, the technique described in this study is sufficient to serve for this purpose. For example, as will be shown in Section 4.3, the change of the crack growth rates occurring with the transgranular/intergranular transition in cracking modes was unambiguously monitored in Type 304 stainless steel in BWR environments.
4.2.3.2 Effect of Environment on The Fatigue Crack Growth Behavior of Inconel 600

Inconel 600 is a passive material with good corrosion-resistance nature. This property can be reflected in the corrosion fatigue crack growth behavior. At frequencies of 0.1 and 1 Hz, the corrosion fatigue crack growth rates observed in this study for different testing conditions are almost the same. Figure 67 shows that the FCGR rates in air at 200°C were the same as those determined at room temperature at a frequency of 1 Hz. From these results, it is apparent that the fatigue crack growth rates in the as-received Inconel 600 in air are not sensitive to temperature.

As shown in Figure 68, the presence of 0.01 M H$_3$BO$_3$ 0.001 M LiOH solution did not exert any environmental acceleration in the fatigue crack growth rates in the as-received Inconel 600. Despite the increase in the solution temperature from 100°C to 250°C, the crack growth rates did not change at the frequency studied. In other words, there was no temperature effect on the fatigue crack growth rates in this environment.

It was mentioned previously in Section 2.6 that the presence of oxygen in aqueous solutions may shift the
corrosion potential about 700 mV in the positive direction. It is obvious that the dissolved oxygen significantly affects the electrochemical behavior of Inconel 600. Although the solution used in the 100°C test was deaerated, the fatigue cracks exhibited the same growth rates as those obtained in air saturated solutions. The lack of the contribution to the crack growth rates with the existence of oxygen in the latter cases is mainly due to the high loading frequency. At high loading frequencies, the fatigue crack growth is purely a mechanical process. Because the environmental enhancement of crack growth rate is time-dependent for both dissolution and hydrogen-assisted cracking mechanisms, the contribution of environmentally-assisted crack growth per loading cycle is dependent upon the time of each loading cycle. If the dissolution rate of metal at the crack tip is very slow, or the critical concentration of hydrogen necessary for hydrogen embrittlement is high, then the time required for a comparable environmental contribution should be long, i.e. a very low loading frequency should be required. Otherwise, the environment will have negligible effect on the da/dN vs ∆K results. Since Inconel 600 is a good corrosion-resistant material, it is not likely that any acceleration will be observed in the fatigue crack growth rates in the dilute
solution studied at a frequency of 1 Hz, which is relatively high for this material/environment system. Decreasing the frequency to 0.1 Hz was not sufficient to cause any environmental effects on the crack growth rates, as shown in Figure 69.

Scanning electron microscope examinations of the fracture surfaces of Inconel 600 fatigued in various environments only showed transgranular cracking mode. In air tests, other investigators had observed intergranular cracking in thermally treated (24 hours at 649°C after solution annealing at 1093°C for 1 hour) Inconel 600 under cyclic loading conditions. However, no evidence of intergranular fracture was found in this investigation. This could be due to the difference in the thermal history of the specimens used.

In 0.01 M $\text{H}_3\text{BO}_3 + 0.001 \text{ M LiOH}$ solution, the fatigue cracks in mill-annealed Inconel 600 also grew transgranularly. The fractographic results is in good agreement with the macroscopic crack growth results. Both showed that the environment did not significantly take part in the fatigue crack propagation processes, at least at frequencies higher than 0.1 Hz. Speidel (39) found that the rate of IGSCC in Inconel 600 in molten NaOH was so low that
it could not contribute significantly to the overall corrosion fatigue crack growth rate until the loading frequency was decreased below $10^{-3}$ Hz. Similarly, it is believed that low loading frequencies would have to be used before a measurable influence of $0.01 \text{ m } \text{H}_3\text{BO}_3 + 0.001 \text{ m } \text{LiOH}$ on the fatigue crack growth behavior of Inconel 600 could be observed.
4.3 Effect of Potential on the Corrosion Fatigue Crack Growth Rate in Type 304 Stainless Steel in Sodium Sulfate Solution at 250 C

4.3.1 Polarization Behavior

Figure 71 illustrates a potentiodynamic polarization curve for sensitized Type 304 stainless steel in deaerated 0.01 m Na₂SO₄ solution at 250 C. The steel exhibits a weak active to passive transition at -600 mVₘ, and a transpassive transition at approximately 200 mVₘ. The general features exhibited by the polarization curve have been reported previously (134). The potentials which were applied in the corrosion fatigue tests are also indicated in Figure 71.

4.3.2 Fatigue Crack Growth Rates

The FCG rates in solution-annealed and sensitized Type 304 stainless steel at 250 C in air at a frequency of 1 Hz are shown in Figure 72. The results indicate that under these conditions, the fatigue crack growth rate is independent of the heat treatment applied to the steel.

The effect of environment and frequency on the fatigue crack growth rate in sensitized Type 304 stainless steel in 0.01 m Na₂SO₄ solution at 250 C under open circuit potential (-665 mVₘ) conditions is shown in Figure 73. These data show
Figure 71 Potentiodynamic polarization curve for sensitized Type 304 S.S. in 0.01 m Na₂SO₄ solution at 250 °C.
Figure 72 Fatigue crack growth rates in solution-annealed and sensitized Type 304 S.S. in air at 250°C and at a frequency of 1 Hz.
Figure 73  Effect of environment and frequency on the fatigue crack growth rates in sensitized Type 304 S.S. in 0.01 m Na₂SO₄ solution at 250 C and at the open circuit potential.
that the FCG rates in deaerated 0.01 \text{ m Na}_2\text{SO}_4 \text{ solution at a frequency of 1 Hz were slightly higher than those determined in air. However, the values for } \frac{da}{dn} \text{ (crack extension per cycle) obtained at 0.02 Hz were almost two times higher than those obtained in the 1 Hz test at equivalent stress intensity ranges. The dependence of } \frac{da}{dn} \text{ on frequency at open circuit potential and at } \Delta K = 20 \text{ Mpa } \sqrt{m} \text{ is shown in Figure 74.}

The variation of crack growth rate with frequency can also be analyzed in terms of the dependence of } \frac{da}{dn} \text{ (crack growth rate) on } f \text{ (frequency). The relationship between } \frac{da}{dt} \text{ and frequency for } \Delta K \text{ values of 20 Mpa } \sqrt{m} \text{ and 25 Mpa } \sqrt{m} \text{ are shown in Figure 75. These data show that the crack growth rates in } 0.01 \text{ m Na}_2\text{SO}_4 \text{ solution at 250 C become increasingly greater than the corresponding cycle-dependent fatigue crack growth rates (represented by the dashed lines) as the loading frequency decreases.}

Corrosion fatigue crack growth rates in sensitized Type 304 stainless steel at a frequency of 1 Hz under controlled potential conditions are depicted in Figure 76. The FCG rates at all potentials, except 200 mV\text{H}, were found to be the same as those determined under open circuit (i.e. free corrosion) conditions. At 200 mV\text{H}, however, there was an
Figure 74 Effect of frequency on the fatigue crack growth rates in sensitized Type 304 S.S. in 0.01 m Na₂SO₄ solution at the open circuit potential (−665 mVₜₚ) and 35 mVₜₚ, and ΔK = 20 Mpa√m, T = 250 C.
Figure 75 Effect of frequency on the time-based crack growth rates in sensitized Type 304 S.S. in 0.01 m Na$_2$SO$_4$ solution at 250 C and at $K = 20$ Mpa m and $K = 25$ Mpa m.
Figure 76 Effect of potential on the fatigue crack growth rates in sensitized Type 304 S.S. in 0.01 m Na₂SO₄ solution at 250 C and at a frequency of 1 Hz.
enhancement of the FCG rates at $\Delta K$ values below 20 MPa$\sqrt{m}$. The variation of the corrosion fatigue crack growth rate with potential at a frequency of 1 Hz and at a constant $\Delta K$ value is shown in Figure 77. The crack extension per cycle at 1 Hz was found to be essentially independent of potential over the range of $-665 \text{ mV}_h$ to $200 \text{ mV}_h$.

Figures 78 and 79 show the resulting corrosion fatigue crack growth rates in sensitized Type 304 stainless steel at frequencies of 0.2 and 0.08 Hz, respectively. The potentials investigated in both cases were $-665 \text{ mV}_h$ (open circuit potential) and $+35 \text{ mV}_h$. At a frequency of 0.2 Hz, the effect of potential on the corrosion fatigue crack growth rate became distinguishable. The values of $da/dN$ at $35 \text{ mV}_h$ were higher than those determined at open circuit potential. The effect of potential became more pronounced as the frequency was decreased to 0.08 Hz. The variations of corrosion fatigue crack growth rates with potentials at 0.2 and 0.08 Hz, $da/dN$ increases with increasing potential, are also demonstrated in Figure 77.

The effect of potential on the fatigue behavior at 0.02 Hz is shown by the data plotted in Figure 80. Clearly, the fatigue crack growth rate at this frequency is potential dependent, at least in the potential region between $-450 \text{ mV}_h$.
Figure 77  Corrosion fatigue crack growth rates in sensitized Type 304 S.S. as a function of potential and frequency in 0.01 m Na₂SO₄ at ΔK = 20 Mpa√m, T = 250 C, open symbol denotes transgranular mode of cracking, half-filled symbol denotes mixed transgranular/intergranular mode of cracking, and filled symbol denotes intergranular mode of cracking.
Figure 78 Effect of potential on the fatigue crack growth rates in sensitized Type 304 S.S. in 0.01 m Na$_2$SO$_4$ solution at 250 C and at a frequency of 2 x $10^{-1}$ Hz.
Figure 79 Effect of potential on the fatigue crack growth rates in sensitized Type 304 S.S. in 0.01 m Na₂SO₄ solution at 250 C and at a frequency of 8 x 10⁻² Hz.
Figure 80 Effect of potential on the fatigue crack growth rates in sensitized Type 304 S.S. in 0.01 m Na$_2$SO$_4$ solution at 250°C and at a frequency of $2 \times 10^{-2}$ Hz.
and $-200 \text{ mV}_H$. The dependence of $\frac{da}{dN}$ on potential at this lower frequency is more clearly shown in Figure 77. These data demonstrate that a significant enhancement of the FCG rate occurs at potentials between $-450 \text{ mV}_H$ and $-200 \text{ mV}_H$. Above this critical range, the crack growth rates are almost constant, but are approximately twenty times higher than those determined at the open circuit potential and at applied potentials below the critical region.

At 250°C and at a frequency of 0.008 Hz, the FCG rates of sensitized Type 304 stainless steel in 0.01 m $\text{Na}_2\text{SO}_4$ solution at two potentials ($-450 \text{ mV}_H$ and $+35 \text{ mV}_H$) are demonstrated in Figure 81. Again, the FCG rates are much higher at potential ($35 \text{ mV}_H$) above the critical range. Although $-450 \text{ mV}_H$ is below the critical range, the FCG rates at this potential were also dependent upon the frequency (Figure 82).

At a potential of $35 \text{ mV}_H$, the FCG rates at different frequencies are summarized in Figure 83. The data plotted in this figure demonstrate that the corrosion fatigue crack growth rates in sensitized Type 304 stainless steel in dilute sulfate solution at potential above the critical range are strongly dependent upon the loading frequency. The FCG rate increases by almost two orders of magnitude as the
frequency decreases from 1 Hz to 0.008 Hz. The values of \( \frac{da}{dN} \) at \( \Delta K = 20 \text{ MPa} \sqrt{m} \) taken from Figure 83 are also shown in Figure 74. As shown in Figure 74, the frequency has a pronounced influence on the FCG rate at 35 mV, while it has less effect at open circuit potential.

The time-based crack growth rates at \( \Delta K = 20 \text{ MPa} \sqrt{m} \) and at \(-665 \text{ mV} \) and 35 mV are presented in Figure 84. Unlike the open circuit potential condition, the crack extension rates at 35 mV are roughly constant \((\sim 6 \times 10^{-8} \text{ m/sec})\) at different frequencies.

### 4.3.3 Fractography

The fracture surfaces obtained at low frequencies at potentials above -450 mV were found to be heavily corroded compared with those obtained at lower potentials and/or higher frequencies.

At the lower frequency of 0.02 Hz, extensive crack branching was observed, but only at potentials higher than -200 mV (Figure 85). However, the extent of branching decreases with decreasing potential above the critical range. Interestingly, the crack length at which branching occurs was found to increase with applied potential. Since multiple-branching was observed in many of the tests, the
Figure 81 Effect of potential on the fatigue crack growth rates in sensitized Type 304 S.S. in 0.01 m Na$_2$SO$_4$ solution at 250 C and at a frequency of 8 x 10$^{-3}$ Hz.
Figure 82 Effect of frequency on the corrosion fatigue crack growth rates in sensitized Type 304 S.S. in 0.01 m Na₂SO₄ solution at a potential of -450 mVₜₜ. 
Figure 83 Effect of frequency on the corrosion fatigue crack growth rates in sensitized Type 304 S.S. in 0.01 m Na₂SO₄ solution at a potential of 35 mV_H.
Figure 84 Effect of frequency on the time-based fatigue crack growth rates in sensitized Type 304 S.S. at open circuit potential (−665 mV_H) and 35 mV_H, ΔK = 20 Mpa√m.
PCG rates given in Figures 80 and 81 include only those results up to the stress intensity at which multiple-branching started to develop.

SEM fractographs of the fracture surfaces for solution-annealed and sensitized Type 304 stainless steel fatigued in air are illustrated in Figure 86. Only transgranular cracks were observed. A significant number of voids were found on the fracture surface. Those voids presumably formed around inclusions. The voids were elongated with the principal axis parallel to the crack propagation direction. EDAX examination showed that the inclusions have high Mn contents, and hence they are believed to be manganese sulfides. As noted by other investigators (162), voids become more evident at higher $\Delta K$ values where void coalescence is favored to occur.

At the open circuit potential, and at frequencies ranging from 1 to 0.08 Hz, the fatigue cracks in sensitized Type 304 stainless steel in 0.01 m $\text{Na}_2\text{SO}_4$ solution at 250 C propagated in a transgranular manner (Figure 87). However, the fracture morphology observed under the same conditions at a frequency of 0.02 Hz exhibited some intergranular features as shown in Figure 88. Fatigue striations were evident on the fracture surfaces of this specimen (Figure
Figure 85  Photograph showing crack branching in a specimen fatigued in 0.01 m Na$_2$SO$_4$ solution at a frequency of $2 \times 10^{-2}$ Hz and a potential of -200 mV$_H$. T = 250 C.
Figure 86 Fracture surfaces of Type 304 S.S. after fatigue cracking in air at a frequency of 1 Hz: (a) solution-annealed, (b) sensitized, T = 250°C.
Figure 87 Fracture surfaces of sensitized Type 304 S.S. after fatigue cracking in 0.01 m Na₂SO₄ solution at the open circuit potential (-665 mV_H), and at a frequency of 2 x 10⁻¹ Hz.
Figure 88 Fracture surfaces of sensitized Type 304 S.S. after fatigue cracking in 0.01 m Na$_2$SO$_4$ solution at the open circuit potential (-665 mV$_{oc}$) and at a frequency of $2 \times 10^{-2}$ Hz: (a) $\Delta K = 19$ Mpa/$\sqrt{\text{m}}$, (b) $\Delta K = 26$ Mpa/$\sqrt{\text{m}}$, $T = 250$ C.
Figure 89  Fatigue striations on the fracture surface of sensitized Type 304 S.S. after fatigue cracking in 0.01 m Na$_2$SO$_4$ solution at the open circuit potential (-665 mV$_{H}$) and at a frequency of $2 \times 10^{-2}$ Hz, T = 250 C.
The average striation spacing is about 0.5 microns, which is consistent with the measured macroscopic crack growth rate of 0.1-1.5 μm/cycle.

The fracture surfaces, which were obtained at 1 Hz at various applied potentials and ΔK ranges, exhibited intergranular facets at the edges of the specimen, as shown by the fractographs in Figure 90, even though the principal mode of fracture was transgranular. At a potential of 200 mV, however, a mixed mode of fracture was also observed near the precrack (Figure 90).

At a potential of 35 mV, the fracture morphology was found to change gradually from the transgranular to intergranular mode as the frequency was decreased from 1 Hz to 0.08 Hz (Figure 91). Mixed transgranular/intergranular fractures were observed at 0.2 Hz while a pure intergranular mode of cracking was found at 0.08 Hz.

At a frequency of 0.02 Hz, the fracture surfaces fatigued at -450 mV exhibited mixed transgranular/intergranular morphology similar to that found at the open circuit potential (Figure 92). However, the percentage of intergranular cracking at -450 mV was significantly higher than that observed at the open circuit potential. Only intergranular cracking was observed in the entire fracture
surface at potentials higher than $-450 \text{ mV}_H$, as illustrated in Figure 93.

Similar fractographic results were found for specimens fatigued at a frequency of 0.008 Hz. An intergranular mode of cracking was observed at a potential of $35 \text{ mV}_H$, while mixed transgranular/intergranular cracking was found at $-450 \text{ mV}_H$. Interestingly, the amount of intergranular cracking in the latter case was drastically increased as compared with that observed on the fracture surface fatigued at a frequency of 0.02 Hz.

4.3.4 Discussion

The effect of environment on the fatigue crack growth rate can be easily recognized by examining either the correlations between $\frac{dA}{dN}$ and $\Delta K$ or the correlations between $\frac{dA}{dt}$ and $f$ (frequency). If the fatigue crack propagates in a cycle-dependent manner (i.e. with no environmental enhancement), then the fatigue propagation rate $\frac{dA}{dN}$ at each $\Delta K$ will have the same value for different cyclic loading frequencies. Accordingly, the time-based log ($\frac{dA}{dt}$) vs log ($f$) correlation will be linear, with a slope equal to one. On the other hand, if an environmental (i.e.
Figure 90 Fracture surfaces of sensitized Type 304 S.S. after fatigue cracking in 0.01 m Na$_2$SO$_4$ solution at a frequency of 1 Hz and under controlled potentials: (a) Edge, $\Delta K = 25$ Mpa/\( \sqrt{\text{m}} \), $+35$ mV$_H$, (b) Center, $\Delta K = 25$ Mpa/\( \sqrt{\text{m}} \), $+35$ mV$_H$, and (c) $\Delta K = 20$ Mpa/\( \sqrt{\text{m}} \), $+200$ mV$_H$, $T = 250$ C.
Figure 91  Effect of frequency on the fracture morphology of sensitized Type 304 S.S. after fatigue cracking in 0.01 m Na$_2$SO$_4$ solution at 35 mV$_{H^+}$: (a) 1 Hz, (b) 2 x $10^{-1}$ Hz, and (c) 8 x $10^{-2}$ Hz, T = 250 C.
Figure 92 Fracture surfaces of sensitized Type 304 S.S. after fatigue cracking in 0.01 m Na$_2$SO$_4$ solution at -450 mV$_H$ and at a frequency of $2 \times 10^{-2}$ Hz: (a) Edge, $\Delta K = 16$ Mpa/$\sqrt{m}$, (b) Center, $\Delta K = 21$ Mpa/$\sqrt{m}$, $T = 250$ C.
Figure 93 Fracture surfaces of sensitized Type 304 S.S. after fatigue cracking in 0.01 m Na$_2$SO$_4$ solution at -200 mV$_H$ and at a frequency of 2 x 10$^{-2}$ Hz: (a) Edge, $\Delta K = 18$ Mpa$\mu$m, (b) Center, $\Delta K = 23$ Mpa$\mu$m, $T = 250$ C.
time dependent) contribution is important, the value of \( \frac{da}{dN} \) for each \( \Delta K \) will increase with decreasing loading frequency, and the log (\( \frac{da}{dt} \)) vs log (f) curve will deviate upwards from a straight line at low frequencies.

As shown in Figure 73, a slight enhancement of the FCGR rates in sensitized Type 304 stainless steel at 1 Hz was observed due to the presence of dilute sodium sulfate solution. However, this enhancement was so small that crack growth appears to be predominantly cycle-dependent, yielding transgranular fractures similar to those observed in air. As shown in Figure 75, the log (\( \frac{da}{dt} \)) vs log (f) curves deviate from this cycle-dependent behavior at low frequencies, which demonstrates the existence of an environmental contribution which increasingly predominates as the frequency is lowered. Ultimately, \( \frac{da}{dt} \) is expected to become constant (i.e. independent of frequency) as the frequency tends to zero. This lower limit may be considered as the stress corrosion cracking rate at the given stress intensity. The stress corrosion cracking rate, \( \frac{da}{dt} \)\(_{SCC} \), can also be estimated using a modified (41) Wei and Landes (31) model (Equation 14). The corrosion fatigue crack growth rate at a frequency of 1 Hz was arbitrarily taken as the true corrosion fatigue crack growth rate in this study. The values of \( \frac{da}{dt} \)\(_{SCC} \) at \( K_{max} \) of 30, 40, and 50 Mpa\( \sqrt{m} \)
were determined from the data reported here to be approximately $2 \times 10^{-10}$, $6 \times 10^{-9}$, and $3 \times 10^{-8}$ m/sec, respectively. These results are in reasonable agreement with the values determined by other authors (161-162) for pure stress corrosion cracking.

At a potential of 35 mV$_H$, the effect of frequency on the corrosion fatigue crack growth rates in sensitized Type 304 stainless steel in 0.01 m Na$_2$SO$_4$ at 250 C becomes more prominent, as indicated by the results plotted in Figures 74 and 83. This is possibly due to the fact that the environment becomes more aggressive at this anodic potential, and chemical attack plays an important role in the cracking process. The results shown in Figure 84 indicate that the time-based crack propagation rates at 35 mV$_H$ are almost independent of frequency. According to the argument of Gallagher (32), the frequency-independent crack growth rate may be regarded as the stress corrosion cracking rate. Based on the results obtained in this study (Figure 84), it is suggested that $(da/dt)_scc$ for sensitized Type 304 stainless steel in 0.01 m Na$_2$SO$_4$ at 250 C and 35 mV$_H$ is about $6 \times 10^{-8}$ m/sec for $K_{max} = 40$ Mpa$\sqrt{m}$.

An important finding of the present study is the existence of a critical potential for environmentally
enhanced fatigue cracking of sensitized Type 304 stainless steel in sulfate solution at 250 C. A similar critical potential has been observed for SCC in this environment (132), as indicated by slow strain rate tests. The results obtained in the present study indicate that the critical potential lies between -450 mV_n and -200 mV_n, which is consistent with the value found for stress corrosion cracking (-400 mV_n to -300 mV_n).

The effect of potential on the corrosion fatigue life of sensitized Type 304 stainless steel in dilute sodium sulfate solution at 250 C can be recognized from the data shown in Figure 94 as well. At a frequency of 0.02 Hz and under the same loading conditions, the number of loading cycles required to grow the same length of fatigue cracks is much more at -450 mV_n than that at 35 mV_n. In other words, the corrosion fatigue life, in terms of number of loading cycles, is greatly reduced when the potential is held above the critical range.

The applied potential affects not only the fatigue crack growth rate but also the fracture morphology. The influence of potential on the fracture surface at a frequency of 0.02 Hz can be seen by examining the photographs shown in Figure 95. At open circuit potential
Figure 94  Results of crack length (a) vs number of loading cycles (N) of sensitized Type 304 S.S. fatigued in 0.01 m Na$_2$SO$_4$ solution at: (1) $2 \times 10^{-1}$ Hz, 35 mV$_H$, (2) $2 \times 10^{-2}$ Hz, 35 mV$_H$, (3) $2 \times 10^{-2}$ Hz, $-450$ mV$_H$, $T = 250$ C.
Figure 95 Photographs of the fracture surfaces of sensitized Type 304 S.S. after fatigue cracking in 0.01 m Na₂SO₄ solution at a frequency of $2 \times 10^{-2}$ Hz, and at open circuit potential (-665 mV<sub>H</sub>) and 35 mV<sub>H</sub>, T = 250°C.
(-665 mV, ) the fatigue crack surface is rather "smooth", while it is very rough, which is due to severe chemical attack, at 35 mV. Moreover, a transition of the cracking mode from transgranular to intergranular occurs as the potential increases to above the critical range. The results shown in Figure 77 suggest that the higher crack growth rate at low frequencies and above the critical potential is associated with the grain boundary corrosion of the sensitized material.

It has been long recognized that the electrochemical conditions within a crack could be quite different from that in the bulk solution. The existence of a critical potential for IGSCC, and the enhancement of corrosion FCGR rates at more positive potentials, probably can be attributed to the crack tip electrochemistry. Unfortunately, our knowledge of the electrochemistry at the tip of a growing crack, particularly at high temperatures, is very limited. In their study of the crevice corrosion of Inconel 600 and Type 304 stainless steel in high temperature aqueous environments, Taylor (163) and Taylor and Silverman (164-165) found that the pH in the crack was lower than that in the bulk solution. It is very likely that the pH at the tip of a growing crack could also be significantly different from that in the bulk solution, particularly at low frequencies.
where pumping action is minimal. This hypothesis is in agreement with the calculations performed by Trumbull (166), who found that despite enhancement of the mass transport of oxygen at the fatigue crack resulting from the displacement of the crack walls, the concentration of oxygen at the crack tip was naturally zero. Hence, the crack tip is anodic compared with the crack walls, and local acidification of the crack tip by cation hydrolysis is expected:

\[ M + 2H_2O = M(OH)_2 + 2H^+ + 2e^- \]

Intergranular stress corrosion cracking in sensitized austenitic stainless steel can be attributed to chromium depletion at the grain boundaries due to precipitation of chromium carbides (167). Indig and McIlree (168) found that at high temperatures, the current densities for alloys, which simulate the chromium-depleted grain boundaries were higher than that of Type 304 stainless steel in both the active and the passive regions of potentials measured in neutral sodium sulfate solution. Their results are illustrated in Figure 96. Taking into consideration the fact that the corrosion rate of low Cr alloy steel (a chromium depleted zone) was higher than that of high Cr alloy, and that acidic environments were formed at the crack tip, Smialowska and Cragnolino (123) suggested that the critical potential for IGSCC in sensitized austenitic stainless steel
Figure 96 Effect of chromium content on the anodic polarization behavior of Fe-Cr-Ni alloys in deaerated water containing 0.01 N Na₂SO₄ at 288 C. (Reference 131)
in neutral solutions corresponded to the potential range over which the active peak appeared in the anodic polarization curve for low Cr alloy in a low pH environment. These arguments also account for the existence of a critical potential for intergranular corrosion fatigue, as observed in this study.

The existence of a critical potential for corrosion fatigue crack growth behavior of sensitized Type 304 stainless steel seems dependent upon the loading frequency or loading rate. In slow strain rate tests, it has also been found that there exists an upper limit of strain rate above which stress corrosion cracking will not occur, whether or not film-rupture event takes place (169-171) or is induced by hydrogen (171). The existence of an upper limit on the strain rate results from insufficient crack advances relative to the amount of strain occurring in the substrate, such that a crack geometry can not be developed and maintained (175). However, in the study of corrosion fatigue crack growth rate using precracked specimens, the dependence of the critical potential on frequency is in turn dependent upon the relative magnitudes of the environmental component and the mechanical component of the crack extension rate. At higher frequencies the rate of crack advancement attributable to the environment is less
than that caused by mechanical forces, but at lower frequencies the crack extension per loading cycle due to chemical attack is comparable to or even greater than the mechanical component, depending upon the potential. Therefore, the existence of a critical potential becomes prominent at low loading frequencies.

It has also been demonstrated by several investigators (172-173) that the crack may experience a potential drop under open circuit or applied potential conditions. The variation of the potential within a crack may affect the stress corrosion cracking or corrosion fatigue crack growth behavior. However, the specific role of the potential variation on the cracking process is not well understood, and more work is necessary to assess the influence of applied potential on the cracking problem.
Chapter V
CONCLUSIONS

5.1 CORROSION FATIGUE CRACK GROWTH IN TYPE 403 STAINLESS STEEL

1. Sodium phosphate and sodium silicate induced minor changes in the electrochemical behavior of Type 403 stainless steel in 10 m NaOH, whereas they had a significant effect on the electrochemical behavior of Type 403 stainless steel in deaerated concentrated sodium chloride solutions. These compounds shifted the corrosion potential in the cathodic direction and expanded the range of the passive region. The effect of these two compounds in sodium chloride solution was due to the increase in pH.

2. Saturated sodium chloride solution (6.6 m) was more aggressive than concentrated sodium hydroxide solution (10 m) with respect to fatigue crack growth rate in Type 403 stainless steel, probably because the former had lower pH. The corrosion fatigue crack growth rate was frequency dependent in both environments, and increased with decreasing frequency.

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3. Sodium phosphate and sodium silicate at the concentrations tested had no inhibitory effect on the fatigue crack growth rates in Type 403 stainless steel in 10 m sodium hydroxide solution at 1.0 Hz and 100 C.

4. At a frequency of 1 Hz and at 100 C, the addition of 0.1 m sodium phosphate or sodium silicate to 6 m sodium chloride solution enhanced the PCG rates slightly. However, at a frequency of 10 Hz and at 100 C, the addition of 0.5 m sodium phosphate or 0.5 m sodium silicate reduced the corrosion fatigue crack growth rates to the level obtained in air, again due to the increase in pH.

5.2 CORROSION FATIGUE CRACK GROWTH IN INCONEL 600

1. The fatigue cracks in Inconel 600 tested in air at 25 C and 200 C had the same growth rates at a frequency of 1 Hz.

2. At a frequency of 1 Hz, no environmental effect on the fatigue crack growth rates in Inconel 600 was observed in 0.01 m H₃BO₃ + 0.001 m LiOH solution at temperatures ranging from 100 C to 250 C.
3. At 200°C, the fatigue cracks in Inconel 600 in simulated PWR primary environments had the same growth rates at frequencies of 0.1 and 1 Hz. Only transgranular morphology was observed on the fracture surfaces of Inconel 600 after fatigue cracking in both air and 0.01 M H₃BO₃ + 0.001 M LiOH solution, and at frequencies of 0.1 and 1 Hz.

5.3 CORROSION FATIGUE CRACK GROWTH IN TYPE 304 STAINLESS STEEL

1. Fatigue crack growth rates in sensitized Type 304 stainless steel were enhanced by the presence of 0.01 M Na₂SO₄ solution. The environmental effect increased with decreasing frequency.

2. At a frequency of 1 Hz, and at all applied potentials, fatigue cracks in sensitized Type 304 stainless steel propagated at the same rates as those determined at the open circuit potential. However, the influence of potential on the FCG rates becomes important as the frequency decreases.

3. At lower frequencies (below 0.08 Hz), there exists a critical potential (between -450 mVₐ and -200 mVₐ) above which the FCG rate in sensitized Type 304 stainless steel was greatly enhanced over that observed at lower potentials.
4. The frequency dependence of the corrosion FCG rate in sensitized Type 304 stainless steel at 35 mV, is greater than that at open circuit potential.

5. The fracture morphology of sensitized Type 304 stainless steel was dependent upon the potential as well as the frequencies. At low potentials and/or high frequency, transgranular cracking was the principal mode of failure; however, at high potentials and/or at low frequencies, fatigue cracks propagated intergranularly.
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