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WELCH, GARY ARTHUR
THE EFFECTS OF TEMPERATURE AND DISSOLVED OXYGEN ON THE STRESS CORROSION CRACKING SUSCEPTIBILITY OF TYPE 304 STAINLESS STEEL IN HIGH-TEMPERATURE, HIGH PURITY WATER.
THE OHIO STATE UNIVERSITY, PH.D., 1978
THE EFFECTS OF TEMPERATURE AND DISSOLVED OXYGEN
ON THE STRESS CORROSION CRACKING SUSCEPTIBILITY
OF TYPE 304 STAINLESS STEEL
IN HIGH TEMPERATURE, HIGH PURITY WATER

DISSertation

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

By


* * * * * * *

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1978

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This dissertation is dedicated to my entire family.

To my mother and father who enabled me to attend college.

To my loving wife Barbara, whose patient support, encouragement, and typing skill helped make it all possible.
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1.0 INTRODUCTION

The purpose of this investigation was to critically study the stress corrosion cracking (SCC) behavior of sensitized and annealed Type 304 stainless steel in an oxidizing environment. Research in this area would be of interest to many segments of the industrial community as well as to the scientific world.

The problem of intergranular stress corrosion cracking (IGSCC) plagues many industries including chemical, nuclear, agricultural, petroleum, automotive, paper, steel, etc. Wherever sensitized stainless steel comes in contact with an oxidizing environment the possibility of IGSCC exists and must be considered.

The environment selected for use in this investigation was high purity water at temperatures from 100°C to 300°C. The specimens were tested using the constant extension rate method of testing (CERT). The primary variables were strain rate, temperature, and the dissolved oxygen concentration of the water.

The open circuit potentials of specimens undergoing IGSCC and TGSCC were also monitored. These potentials in combination with existing electrochemical data made possible the formulation of models which explain and predict the observations.

The dissertation is divided into four main sections. The literature survey provides the necessary background information. The section
entitled "Materials, Equipment, and Procedure" describes the materials, experimental apparatus, and experimental procedures used in the course of the investigation. The results are included in the third main section and a discussion of the results follows.

Within the section entitled "Discussion of Results", processes are outlined which can explain the IGSCC which was observed at high dissolved oxygen concentrations; the transgranular stress corrosion cracking (TGSCC) which was observed at intermediate dissolved oxygen concentrations; and the dual mode stress corrosion cracking observed at intermediate dissolved oxygen concentrations. The effects of strain rate, temperature, and dissolved oxygen concentration on the SCC susceptibility of both annealed and annealed plus sensitized Type 304 stainless steel in high temperature high purity water was determined.
2.0 LITERATURE SURVEY

Stress corrosion cracking as defined by Fontana and Greene (1) refers to cracking caused by the simultaneous presence of a tensile stress and a specific corrosive medium. During stress corrosion cracking, the metal or alloy is virtually unattached over most of its surface while fine cracks progress through it. Excellent reviews dealing with the SCC of austenitic stainless steels have been published by Latanison and Staehle (2), Staehle (3), Theus and Staehle (4), Coriou (5), Berge and Cordovi (6), Nielson (7), Van Droffelaar (8), Sedriks (9), Boyd and Berry (10), Wilson (11), Gulbranson (12), Pugh (13), Hubner and Johanson (14), Coriou and Graill (15), Cheng (16), Berry (17), van Rooyen (18), and Board (19).

The morphology and rate of penetration of SCC depend upon three principal considerations: alloy chemistry, properties of the material, and the influence parameters. A schematic relationship of these factors is shown in Figure 1 (20). The schematic representation of Figure 1 identifies phenomenological parameters. It is not mechanistic, but whatever mechanistic development ensues must lead to a relationship of the type shown in Figure 1 and must account for the quantitative dependences.

The literature survey is organized in the manner depicted by the schematic of Figure 1—Section 2.1 considers the effects of materials' composition and microstructure on crack initiation, crack growth rate, and crack morphology. Section 2.2 considers the effects
(Material) \times (Properties) \times (Influence) =

- Crack Initiation
- Crack Growth Rate
- Crack Morphology

Figure 1

General equation for principal dependences of SCC phenomena. (20)
of the various influences (environmental, mechanical, and physical) on crack initiation, crack growth rate and crack morphology.

2.1 Effect of Alloy Composition and Microstructure on SCC

The first half of this section considers the effects of alloy composition on SCC resistance and the second half considers the effects of the microstructure of the alloy on SCC resistance. Information relating to the composition of the grain boundary regions of these alloys is presented in Sections 2.1.4 and 2.1.6.

2.1.1 Major Alloying Elements

It was beyond the scope of this investigation to determine the effects of various alloying additions to Type 304 stainless steel on the susceptibility to cracking. However, if the effects of various alloying additions of the SCC resistance of an alloy are understood, then it may be possible to extend the range of applicability of previous work that has been done on 304 stainless steel. Natural extensions would be to Type 304 stainless steel and the higher nickel alloys, Inconel 800 and Inconel 600. The elements included under the heading Major Alloying Elements are nickel, chromium, molybdenum, and carbon.

2.1.1.1 Nickel

High nickel alloys are more resistant to chloride cracking than low nickel alloys. Additions of nickel raise the stacking fault energy of austenitic alloys thereby making crack initiation and possibly crack propagation more difficult (21). However, high nickel alloys are more susceptible to cracking in high purity water than intermediate nickel alloys (22).
2.1.1.2 Chromium

Latanison and Staehle (2) concluded that addition of chromium caused a variable effect in chloride solutions: adding between 12 and 25% increased the stress corrosion susceptibility of the alloy while additions above and below this range inhibited it.

As stated by Theus and Staehle (4), the opinion is now that the effect of chromium on the resistance of an iron or nickel base alloy is dependent upon the cracking medium. Sedriks (23) reached the same conclusion, i.e. the effect of chromium on the susceptibility of an alloy is variable.

Chromium also exerts a strong influence on the repassivation kinetics of the alloy (24). Increasing the chromium content decreases the time necessary for repassivation of the alloy to occur following a rupture event. The sluggish repassivation kinetics of low chromium alloys is of particular importance when considering the stress corrosion cracking behavior of sensitized austenitic stainless steels because of the low chromium content present in the chromium depleted zones adjacent to the grain boundaries. This results in a high rate of dissolution adjacent to the grain boundaries. The importance of the effect of chromium on the repassivation kinetics of austenitic stainless steels is discussed in greater detail in Section 2.1.4.

2.1.1.3 Carbon

Both Latanison and Staehle (2) and Sedriks (23) have concluded that carbon is more often than not beneficial to SCC. However, since some instances have been found where carbon additions are detrimental (25), Theus and Staehle (2) conclude that carbon's effect on the SCC
resistance of alloys is variable.

Payer and Staehle (26) conducted an excellent investigation into the dissolution behavior of carbide in aqueous environments. The significant results of the study were:

(1) Although the thermodynamic stability of graphite and the carbides in aqueous environments are similar, the materials react quite differently because of kinetic considerations.

(2) The carbides \( \text{C}_r\text{C}_6 \) dissolved by an electrochemical process.

(3) The dissolution behavior of the carbides is closely related to that of the metal constituent of the carbide.

(4) The dissolution products are a function of the carbide structure and the potential at which dissolution occurs.

(5) The kinetics of the hydrogen reduction reaction vary considerably on the different carbide structures.

The most important result of the investigation by Payer and Staehle (26) is the destruction of the belief that carbides are inherently stable structures. Further discussion of carbide dissolution is included in Section 2.1.4.

2.1.1.4 Molybdenum

Latanison and Staehle (2) concluded that molybdenum has a variable effect on the SCC resistance of austenitic materials. Below 4%, the effect is detrimental, while above 5%, the indications are that molybdenum is beneficial to SCC resistance. According to Theus and Staehle (4), data obtained since the original review does not contradict that conclusion; molybdenum additions have a variable effect on SCC. As
pointed out by Theus and Staehle (4) molybdenum is added to stainless steels to improve their pitting resistance (27). However, molybdenum additions are generally detrimental to SCC while silicon additions are usually beneficial. To further confuse the issue, Type 316 L stainless steel has a major resistance to SCC in high purity water whereas Type 304 L stainless steel is susceptible to SCC in the same environment (28).

2.1.2 Minor Alloying Elements

The elements classified as minor alloying elements for the purposes of this survey include: nitrogen, phosphorus, silicon, sulfur, and manganese.

2.1.2.1 Nitrogen

Adding nitrogen to austenitic stainless steels accelerates the cracking process. There is, however, a relationship between melting practice and SCC susceptibility. Ryabchenkov and Gerasimov (29) found that although nitrogen additions increased an alloy's susceptibility to SCC, alloys that were vacuum melted showed a significant improvement over those that were melted in air.

2.1.2.2 Phosphorus

Phosphorus and the other Group V-A elements are detrimental to the SCC behavior of austenitic materials in acid chloride environments (4). The effects of phosphorus segregation on SCC susceptibility is discussed in Section 2.1.6.

2.1.2.3 Silicon

The statement that silicon additions were beneficial to SCC resistance was thought to be universally true based upon tests in MgCl₂.
solutions (2), (23). When silicon bearing alloys were tested in an alkaline environment (30) and in a high temperature oxygen - chloride environment (31) the alloys were prone to cracking. The exact effect of silicon additions to austenitic alloys is therefore unclear and its effect on SCC resistance must be classified as variable.

2.1.2.4 Sulfur

The most extensive study on the effect of sulfur on SCC resistance was conducted by Kowaka and Fujikawa (32) who expressed the maximum cracking time as a function of sulfur concentration in an 18Cr-10Ni steel. They conclude that sulfur has a variable effect on the SCC resistance on this alloy. Other investigators have found that up to .02% sulfur has had no effect on the cracking behavior of the steels that were tested (33, 34, 29). Theus and Staehle (2) therefore conclude that rather than stating that sulfur is detrimental, it is more accurate to state that sulfur has a variable effect. Additional information on the effects of sulfur, particularly when it is segregated to grain boundaries, is presented in Section 2.2.7.

2.1.2.5 Manganese

Adding more than 2% manganese to austenitic stainless steels is detrimental to SCC resistance.

2.1.3 Physical Metallurgy of Austenitic Stainless Steel

This section deals with the metallurgical structure of austenitic stainless steels. It is my intent to delineate what constitutes a susceptible structure for SCC and which structures are essentially immune to SCC.

The logical point to begin this discussion of the physical metallurgy of the austenitic stainless steels is with the Fe-Cr-Ni terary
system. In steels containing both Cr and Ni, the opposing ferrite forming effect of Cr and the austenite-stabilizing effect of Ni are combined to produce alloys with a wide range of structures. Due to the sluggishness of some of the transformations and the lack of alloy purity in many of the studies, the exact equilibrium situation has at best only been approached. However, technologically, true equilibrium is also seldom approached. Therefore, in many cases, the stainless alloys represent nonequilibrium or, at best, metastable materials (35).

The nature of the martensite transformation which can occur in Fe-Cr-Ni alloys has been studied in great detail. The martensite transformation in the normal austenitic stainless grades normally occurs only upon cooling below room temperature or upon deformation below the \( M_d \) temperature, although it has been found at higher temperatures following the cooling of regions of compositional heterogeneity, such as Cr-depleted grain boundaries (36). As has been pointed out by Cina (37), the transformation, although diffusionless, can occur isothermally or thermally. Eichelman and Hall (38) yielded the following expression for the determination of the \( M_s \) temperature:

\[
M_s \ (°C) = 1302 - 42(\%Cr) - 61(\%Ni) - 33(\%Mn) - 28(\%Si) - 1667(\%(O+N))
\]  

(1)

The equation was empirically formulated for alloys covering the range of 10 to 18% Cr, 6 to 12% Ni, .6 to 5% Mn, .3 to 2.69% Si, .004 to .12%C, .01 to .06% N, balance Fe. The \( M_s \) temperature calculated for the material used in this investigation is -116.8°C.

The \( M_d \), or temperature above which deformation stresses cannot initiate the martensite transformation, can be estimated in like manner. Because of the experimental difficulty associated with measuring the
true $M_d$ of an alloy, Angel (39) defined a temperature, $M_{d30}$ at which 50% martensite is formed in tension in 18-8 type alloys after a true strain of 30%. Angel's expression is:

$$M_{d30}(^\circ C)=413-462((C+H)),-9.2(1/2Si),-8.1(Mn),-13.7(Ca),-9.5(Ni)-18.5(Mo)$$

The $M_{d30}$ temperature for the material used in this investigation is 37.5°C.

Angel concluded that the governing factor in the formation of deformation induced martensite is the supply of mechanical energy through deformation. Stress is of primary importance but strain is also of importance since it affects the local peak stresses which can activate martensite embryos.

When FCC alloys are plastically deformed the dislocation distribution attained depends upon the ease with which dislocations can cross-slip from a $\{111\}$ plane to conjugate slip plane. For cross-slip to occur, a dissociated dislocation has to associate, and the ease with which this can occur depends upon the distance separating the two halves of the partial dislocation. The region between partial dislocation consists of stacking fault and can be looked upon as four layers of hcp material. The energy to produce such a unit area of hcp material four atom layers which is usually called the stacking fault energy (SFE).

Thus, SFE is a measure of the inherent stability of the FCC phase relative to its hcp counterpart. A high SFE implies high inherent stability; a low SFE, an inherent tendency to transform (40). The dislocation distribution is controlled by SFE during plastic deformation and this in turn influences work hardening behavior, creep rate, recovery and recrystallization, the morphology of precipitated phases, and the type of
susceptibility to SCC. Low values of SFE tend to promote co-planar dislocation arrays whereas high SFE values promote dislocation tangles or cell boundaries of dislocations.

Swann (21) points out that concerning transgranular cracking the requirement that short range order must be destroyed by several dislocations moving on the same slip plane in order to provide a site for chemical attack may explain the lack of transgranular cracking in un-stressed alloys and pure metals. This reasoning casts some doubt on the validity of comparing stress corrosion specimens of different composition which have been tested at constant fractions of the flow stress. If the motion of dislocation is important in the nucleation of stress corrosion cracks then the number of dislocations moving and their velocity during a test should be kept constant. This condition would be approximately fulfilled if specimens were compared at stresses necessary to give the same creep rate.

2.1.4 Sensitization of Austenitic Stainless Steel

2.1.4.1 Structural Effects

Intergranular corrosion of stainless steels refers to a localized attack, in certain corrosive environments, at the grain boundaries which results in loss of strength and ductility. This type of corrosion is particularly severe when the steel is treated in the sensitizing range 450-900°C following a solution anneal. Time-temperature-corrosion susceptibility of many austenitic steels exhibits a C-curve behavior with the knee of the curve in the 600-650°C range. A healing effect, the restoration of the corrosion resistance, occurs when the material is treated for prolonged time at the sensitizing temperatures
The primary factors determining the degree of sensitization are: temperature, time at temperature, composition profile, alloy composition, and carbon composition. The influence of these variables on the final structure that is obtained is discussed in this section.

The almost universally accepted theory for intergranular corrosion first proposed by Bain (43) is based upon depletion of chromium in the grain boundary areas. Since Bain's original proposal for Cr depletion as the reason for increased susceptibility, the theory has been refined based primarily on thermodynamic and/or diffusion considerations (44,45, 46,41,47, 48).

The Cr depletion model is based upon the following assumptions (65):

(1) A minimum Cr level is required in stainless steel to have a protective passive film, estimated to be about 12%.

(2) The carbide precipitate contains up to about 95% Cr by weight, whereas the bulk alloy contains only 18%. Thus the surrounding alloy matrix is depleted in Cr.

(3) During the sensitization heat treatment, the bulk diffusion of Cr from the matrix to the depleted region at the grain boundary is too slow to permit replenishment.

(4) If the chromium content is depleted to less than about 12%, the passive film will not form and that material will corrode preferentially.

In temperature range of 450-900°C, Cr$_{23}$C$_6$ (and carbon) is virtually insoluble and precipitates out of solid solution if the carbon content is about .02% or higher. The Cr is thereby removed from solid solution and the result is metal with lowered Cr content in the area adjacent to
the boundaries.

Stawstrom and Hillert (44) assume in their analysis of grain boundary precipitation that a uniform grain boundary composition exists. Tedman, Vermilyea, and Rosolowski (45) have shown that this is inadequate in certain cases. They have shown that patchy grain boundary corrosion bay result as a consequence of large variations in the chromium content in the boundary.

The Stawstrom–Hillert Method also predicts that the carbon solubility in stainless steels increases beyond about 20% chromium. It seems likely that this is a result of the method of calculation (45).

Tedman, Vermilyea, and Rosolowski (45) contend that the chromium content in equilibrium with the carbide particles is a strong function of the steel composition and of the sensitizing temperature and can be predicted by the thermodynamic theory. Because of rapid grain boundary diffusion, the chromium depletion may be reasonably uniform despite a considerable separation of carbide particles. When this "patchy" behavior is encountered it will generally be more pronounced at higher heat-treatment temperatures because of the lower ratio of grain boundary to bulk diffusion coefficient. Their results demonstrate that the degree of sensitivity is controlled primarily by the thermodynamically controlled minimum chromium content, with morphological features of carbide particles playing a secondary role.

Through the modification of an analytical electron microscope system to increase its spatial resolution, Rao and Lifshin (50) have been able to provide direct experimental evidence of Cr depletion at grain boundaries and at carbide–matrix interfaces. Their results are shown in Figures 2, 3, and 4. It is obvious that chromium depletion
Figure 2 (Top)
Composition versus distance from grain boundary - 1121°C/10 min/WQ

Figure 3 (Bottom)
Composition versus distance from grain boundary - 1121°C/10 min/WQ + 677°C/24 hr/WQ (50)
Figure 4

Composition versus distance from carbide centerline - 1121°C/10 min/WQ + 677°C/24 hr/WQ (53)
occurs in the grain boundary region after a sensitization treatment. The wt.% of chromium in the grain boundary region drops below 10%.

Hishida and Nakada (51) provide several time-temperature-sensitization curves along with procedures which allow calculation of the critical cooling rate necessary for sensitization from time-temperature sensitization curves. Solomon (52) describes a procedure for the construction of a continuous cooling sensitization curve from a time-temperature sensitization curve. This procedure predicts the observed behavior within an order of magnitude. Continuous cooling sensitization is more severe than what is predicted from isothermal data. Solomon (52) showed that cooling from 1000°C is less sensitizing than if one cools from 900°C or 800°C. Cooling from 1000°C results in sensitization, as defined by A262E, only when the cooling rate is below .4°C/SCC. In contrast, when the peak temperature is 800°C, sensitization was first detected in specimens cooled as fast as 1.6°C/SCC.

Additional work considering the metallurgical changes occurring during sensitization are listed below:

Berry et al (53) showed that there was no significant difference in stress corrosion response between sensitizing Type 304 stainless steel at 621°C for 7 or for 24 hours in agreement with Clarke and Gordon (25).

Gelling and de Jongh (54), in high temperature microscopy experimentation during the oxidation of austenitic stainless steels, have shown that an increased rate of oxidation is found in a narrow zone along grain boundaries where Cr carbides have been precipitated. This lends support to the Cr-depletion theory of intergranular corrosion.

Vermilyea, Tedman, and Broecker (55) conducted an interesting study concerning the effects of annealing treatments in the temperature range
816 to 1038°C result in a substantial delay in carbide precipitation upon subsequent heating at 593 to 704°C, and consequently the rate of sensitization is appreciably less. It is believed that the delayed sensitization results from slower development of grain boundary carbides.

Tedman and Vermilyea (56) investigated the susceptibility of various stainless steels to intergranular carbide sensitization. According to their study, in order to increase resistance to susceptibility to grain boundary carbide sensitization, the following should be done:

(1) Maximize the chromium content of the alloy.

(2) Minimize the nickel content of the alloy.

(3) Obtain material with the lowest possible carbon content.

There have been several investigations into the mechanism of formation of $M_2\text{C}_6$ carbides in austenite (57, 58, 59). The general conclusions are:

(a) Precipitation occurs on grain boundaries, non-coherent and coherent twin boundaries, and on dislocations.

(b) The main type of grain boundary precipitate forms discontinuously and has a parallel orientation with one of the grains. This orientation is also found for particles which nucleate on dislocations within the grains.

(c) All forms of precipitate have interfaces of the type lll with the matrix. An analysis of the atomic configuration of lll shows that only a small amount of misfit occurs. The interfaces may be considered as being partially coherent.

In a 24% Ni, 25% Cr austenitic stainless steel, Widmannstatten precipitates of needles lying along 110 has been found after quenching from 1150°C and aging at either 650°C or 750°C. The precipitates are in
parallel orientation with the matrix, and are bounded by two conjugate sets of 111 interface planes contained in their growth direction.

It has been shown that phosphorus promotes the nucleation of M23C6 precipitate on 111 matrix planes (60). Phosphorus substitutionally replaces the metal atoms to the precipitate, resulting in a decreased lattice parameter of the precipitate, which seems to favor its increased matrix nucleation, and its lath-like 111 habit.

Aust et al (61,62) suggested that the intergranular corrosion of austenitic stainless steels is associated with the presence of continuous grain boundary paths of either solute segregated regions or second phase particles. Materials in the solution treated condition, which have been quenched from between 1050 to 1300°C, exhibit solute segregation at the grain boundaries which provides a continuous path for attack by the corrosion solution. If the austenitic stainless steel is quenched from 600°C (or from the sensitization heat treatment range of 500 to 700°C) continuous carbides or second phase particles are formed at the grain boundaries thereby producing a large continuous path for classical intergranular corrosion in the sensitized condition. In materials heat treated and quenched from 800 to 900°C, isolated carbides are formed at the grain boundaries. These isolated carbides may incorporate solute impurities drained from the grain boundary region. This latter heat treatment (i.e. quench from 800 to 900°C) should then reduce the intergranular corrosion rate since a discontinuous penetration path for the corrosion medium is now present at the grain boundaries. Also, on the basis of this model, a low corrosion rate would be expected for a high purity material having relatively clean or segregation free
grain boundaries (42).

In the segregation theory, chemical differences between the segregate and the grains supposedly provide the driving force for the corrosive attack. However, Payer and Staehle (26) have shown that carbides are as anodic or more anodic than the materials of which they are composed. It is doubtful that the chemical difference between segregate and grain is sufficient to cause corrosive attack in the system.

Indig and McIlree (63) in studies of the solute segregation model of intergranular attack have shown that extremely oxidizing conditions (1.33 V$_{SHE}$) are necessary for attack to occur.

The electrochemical theory proposed by Stickler and Vinchier (64) and by Kinjell (65) relies on the idea that the carbides are more noble than the metal itself which leads to galvanic action between the two (54). Payer and Staehle (26) have shown that this is not the case and this theory should not be considered.

Streicher (66) and Coriou et al (67) suggest that the strain energy associated with grain boundaries provide the driving force for intergranular corrosion. This idea can be refuted on the basis that strain contributes only tenths of millivolts to the overall potential. This potential is not large enough to account for the observed intergranular attack.

Recently Povich (68) has shown that the sensitization of Type 304 stainless steel occurs at temperatures well below the normal temperature range for sensitization. A prerequisite for this low temperature sensitization is the presence of chromium carbide nuclei along grain boundaries. The potential relevance of low temperature sensitization to
industrial processes is that after many years at process operating temperatures, the degree of sensitization in welded Type 304 stainless steel may progress via low temperature sensitization in welded Type 304 stainless steel may progress via low temperature sensitization to enhance the possibility that IGSCC will occur. Low temperature sensitization enhancement can occur to a significant depletion of chromium within 10 years at 300°C in certain heats of Type 304 stainless steel. A schematic representation of low temperature sensitization is given in Figure 5. In Figure 6 the Arrhenius representation of the low temperature sensitization occurring in Type 304 stainless steel is plotted. The experimental results suggest that low temperature sensitization enhancement can occur to yield a significant depletion of chromium within 10 years at 300°C in certain heats of Type 304 stainless steel.

The so-called stabilized austenitic grades such as Types 321 and 347 stainless steels, have strong carbide formers, such as Ti and Nb, to form preferentially their respective carbides in place of chromium carbide. This eliminates the Cr depleted zone adjacent to the grain boundary.

Whereas the stabilized stainless steels can be made immune to intergranular attack in the sensitized condition, they are susceptible in the welded condition to "knife-line" attack in highly oxidizing media (104). Furthermore, the stabilized grades are usually more difficult to weld successfully, particularly in thicker sections.

2.1.4.2 Chemical Reactivity Associated with Sensitization

The most important result associated with the sensitization of an austenitic stainless steel is the alteration of the chemical reactivity
FIGURE 3 — Schematic representation of low temperature sensitization (LTS). Paths A and B do not cause sensitization. However path C causes severe sensitization. The shaded region is the normal isothermal time-temperature-sensitization (TTS) zone.(68)
FIGURE 6 — Arrhenius representation of the low temperature sensitization of Type 304 stainless steel wire. Wires in the as-received condition were initially given a nucleation heat treatment of 60 minutes at 700 C. Following the nucleation heat treatment, the wires were given vacuum heat treatments for the times and temperatures indicated. The numbers associated with the data points represent the ultimate tensile strength following the heat treatment and exposure to A262E. The straight line was drawn where the UTS ≤ksi. (68)
of the alloy in the grain boundary region. The chromium content within the grain boundary region determines the reactivity of the alloy.

The chromium concentration of the alloy has a decisive influence on the shape of a polarization curve (69, 24,70)(Figure 7 and 8). Chromium reduces the critical passivation current as well as the current in the passive state and in the beginning of the transpassive region. At more positive potentials in the transpassive region chromium increases the current despite the fact that secondary passivation is induced at certain concentrations (16-30%). In austenitic steels, molybdenum reduces the passivation current density and also the corrosion current in the beginning of the passive region. Molybdenum also widens the immunity region and increases the resistance of the steel in the active state. Nickel increases the resistance in the anode overvoltage and therefore increases the resistance in the active state. However, with increasing nickel concentrations the critical passivation current density increases somewhat.

The effects of the chromium content of the alloy are clearly depicted by the polarization curves shown in Figures 7 and 8. The effect of temperature on the polarization curves is also shown. In general an increase in temperature results in an increase in the observed current density. The results depicted in Figures 7 and 8 indicate that the current density within the chromium depleted region of a grain boundary could be three orders of magnitude greater than that of the bulk material. The small area on which this high current is located prevents the material from dissolving rapidly due to general corrosion although this highly localized elevated current density leads to intergranular attack.
Figure 7
Potential-current density curves in 2N $\text{H}_2\text{SO}_4$ at 25°C (24).

Figure 8
Potential-current density curves in 2N $\text{H}_2\text{SO}_4$ at 90°C (24).
As described in Section 2.1.4.1 the chromium depleted zone results from the precipitation of $\text{Cr}_2\text{C}_6$ within the grain boundaries and the subsequent depletion of the chromium concentration in the adjacent areas. It is a popular misconception that the precipitated carbides are inherently more noble than the surrounding matrix. Payer and Staehle (26) have demonstrated how the chromium carbides are at least as active and possibly more active than the matrix.

The section can be summarized in the following manner:

1. Sensitization results in the precipitation of $\text{Cr}_2\text{C}_6$ and a chromium depletion region adjacent to the $\text{Cr}_2\text{C}_6$.
2. The chromium depleted region is more reactive than the matrix. Current densities of the low chromium areas could be as much as three orders of magnitude greater than those of the matrix.
3. The repassivation rate of the material decreases as the chromium content of the alloy decreases.
4. The precipitated chromium carbides are at least as active as the surrounding matrix.

2.1.5 Detecting Sensitization in Stainless Steels

The standard methods used for detecting susceptibility of intergranular attack in stainless steels are described in ASTM standard A262. A262 covers the following five tests:

1. Oxalic Acid Etch Test;
2. Ferric Sulfate-Sulfuric Acid Test;
3. Nitric Acid Test;
4. Nitric-Hydrofluoric Acid Test;
5. Copper Sulfate-Sulfuric Acid Test.
The oxalic acid test is a rapid method of identifying, by simple etching, those specimens of certain stainless steel grades which are essentially free of susceptibility to intergranular attack associated with chromium carbide precipitates.

The ferric sulfate-sulfuric acid test, the nitric acid test, and the nitric-hydrofluoric acid test are based upon weight loss determinations and therefore provide a quantitative measure of the relative performance of specimens evaluated. In contrast, the copper-copper sulfate-sulfuric acid test is based on visual examination of bend specimens and, therefore, classifies the specimens only as acceptable or non-acceptable.

The five methods used for detecting susceptibility to intergranular attack employ specific potentials which are unique to each test. A summary of the range of corrosion potentials expected from these various tests is shown schematically in Figure 9, adapted from Cowan and Tedman (71). The oxalic acid test differs from the other tests in that at potentials above about 1.2V low chromium alloys corrode with a lower current density than high chromium alloys (See Figure 9). Therefore, susceptibility to intergranular corrosion is detected in the oxalic acid test when dissolution of the carbide occurs rather than dissolution of the low chromium region caused by sensitization.

The potentials of the nitric acid test, acid ferric sulfate test, and acid copper sulfate test all fall within the passive region of austenitic alloys. Under these conditions low chromium regions dissolve more rapidly than the matrix. The pH's of these tests are lower than those of the oxalic acid test thereby increasing the dissolution
Figure 9
Range of corrosion potentials expected in tests for sensitization (71)
Clarke, Cowan, and Walker (72) have compared the various methods for measuring the degree of sensitization in stainless steel. The three methods that were investigated were: (a) a modified oxalic acid etch test; (b) a modified copper-copper sulfate-sulfuric acid test; and (c) an electrochemical polarization reactivation method (EPR). Work by General Electric has shown that moderately sensitized materials can undergo intergranular SCC in environments that do not cause appreciable intergranular attack in the absence of stress, such as in the recommended tests for detecting susceptibility to intergranular attack. Therefore a more discerning test for measuring susceptibility to intergranular attack is needed. The results of the investigation by Clarke, Cowan, and Walker (72) indicate that the EPR test may be the needed test. Their conclusions are:

1. The EPR method is considered the most sensitive test for quantitatively measuring the levels of sensitization which are of primary concern to the nuclear industry.

2. All three methods tested are capable of detecting moderate to severe degrees of sensitization in austenitic stainless steel.

3. Both the EPR test and the oxalic acid etch test appear to saturate at the higher degree of sensitization, which results in a loss of discriminating power between different heats of material.

4. The copper-copper sulfate-sulfuric acid test does not saturate, and retains its discriminating power at high degrees of sensitization, but it is not a suitable method for detection at the lower degrees of sensitization.
(5) The EPR method is the most suitable for detecting potential susceptibility to IGSCC, and it is the only technique considered adaptable for obtaining quantitative information in the field nondestructively. For use in industry, a method will be required to correlate the EPR method to the industrial environment of concern if it is to be used as an indication of IGSCC potential rather than as a measure of sensitization caused by grain boundary chromium depletion.

The method that has been used by General Electric to correlate their EPR results with actual environments has been the constant extension rate test (CERT). Their correlation curve is shown in Figure 10. There is a great deal of scatter in the data which is available at this time. Therefore the usefulness of the correlation is questionable at this time. As more data is accumulated and refinements are made in the technique, this procedure should prove to be extremely valuable.

2.1.6 Grain Boundary Segregation

In addition to the carbide precipitation which occurs during the sensitization of austenitic stainless steels. Some segregation of minor alloying elements may occur during the sensitization treatment. If these segregating species can be identified it may be possible to prevent the detrimental effects of the segregation. This section considers the problem of grain boundary segregation.

A grain boundary is defined as the interface between two crystals of the same phase; geometrically it is a surface. The chemical composition and mechanical electrochemical response of the grain boundary and its adjacent matrix can be quite different from that of the bulk matrix because of the segregation of alloying elements and impurities. The driving force for this segregation can be either thermodynamic, i.e.
Figure 10
Correlation between degree of sensitization and IGSCC resistance for 11 heats of Type 304 stainless steel (72)
Gibbs adsorption, or from nonequilibrium or kinetic causes (49). The driving force for Gibbs adsorption is a reduction in the total free energy of the polycrystalline system. If an alloying or impurity element can reduce the grain boundary energy (in energy units per unit area) by being adsorbed into or near to the boundary, there is a driving force for segregation. There is no doubt that Gibbs adsorption occurs, but its result is only additive to other causes of segregation (49).

The driving force for nonequilibrium segregation is a solute-vacancy interaction mechanism proposed by Aust et al (73). This model employs the fact that grain boundaries are sinks for vacancies and other defects. When the metal is undergoing a high temperature anneal, an equilibrium concentration of vacancies is present. There can also be some vacancy-solute binding at this temperature. During the quench or cool down to lower temperatures, the equilibrium number of vacancies is drastically reduced and there is a temporary supersaturation of vacancies. Thus any vacancies within a diffusion distance of the grain boundary will be annihilated at the grain boundary. As the vacancies migrate to the grain boundary they will tend to drag along those solutes whose vacancy-solute binding energy is positive. Thus, effective uphill diffusion of the solute occurs and solute enrichment over the diffusion distance near the boundary area occurs. The solute enrichment occurs atomistically in the form of solute clusters. As vacancy-solute pairs collide, one or more vacancies are released to form a less mobile solute atom complex. More and larger clusters are found as one approaches the grain boundary.
Armijo (74) and Aust et al (75) have shown that significant grain boundary hardening occurs in Type 304 stainless steel which is an indication that significant grain boundary segregation occurs in commercial purity alloys. Knowing that segregation occurs, however, does not tell qualitatively what species are segregating nor what the concentration levels are of the species near the grain boundaries.

Investigations by Armijo (46) and by Coriou et al (76) (77) have shown that addition of P and Si in otherwise high purity alloys resulted in grain boundary hardening and the promotion of intergranular attack in boiling $0.5N HNO_3 + 0.5N K_2Cr_2O_7$ solution. The addition of nitrogen, manganese, sulfur, and oxygen showed no propensity to cause intergranular corrosion. Joshi and Stein (42) measured the chemistry of grain boundaries using Auger Electron Spectroscopy (AES) in Type 304 stainless steel. For the solution-annealed and water-quenched condition, the authors found only sulfur to be a major segregate and found silicon to segregate after annealing at intermediate temperatures. They tested their samples in the Strauss solution (boiling sulfuric acid + $Cu_2SO_4+Cu$) and found that chromium depletion was necessary for susceptibility in the Strauss test and that sulfur segregation was needed to promote nitric-Cr$^{4+}$ susceptibility.

Figure 11 shows an Auger spectrum along with depth-composition profiles, obtained from the fracture surface of a 304 stainless steel which had been preheated at 1250°C for 3 1/2 hours and then reheated at 625°C for 16 days (78). The fracture made of this specimen was ductile but it followed the grain boundaries. A large amount of sulfur was observed along with small amounts of Si and P. The results suggested that a
Fracture Surface Composition
304 Stainless Steel
1250°C 3½ Hr AC +
625°C 16 Days WQ

Figure 11
AES spectrum and composition-depth profiles for a 304 stainless steel heated at 1250°C for 3 1/2 hours followed by water quenching and reheated at 623°C for 16 days (78)
monolayer of sulfur was on the surface of the specimen.

Sulfur segregation was also found by Chaung, Lumsden, and Staehle (78) in 304 stainless steel for the following cases: (a) heated at 1225°C for 116 hours, followed by water quenching; (b) heated at 1300°C for 5 days followed by furnace cooling at a cooling rate of 50°C/hr.

From these results it appears that sulfur segregation occurs for as-quenched, slow cooling, and sensitizing conditions. Therefore sulfur is not the dominating species which determined whether or not 304 stainless steel is susceptible to SCC.

Table 1 presents the results of several investigations into the grain boundary segregation in Fe-Ni-Cr systems (49).

The segregation of alloying elements and impurities to the grain boundary region will have a pronounced effect on both the mechanical properties and the electrochemical behavior of the grain boundary. For the cases of P and S segregation, dissolution at the grain boundaries could lead to localized acidification of the solution as shown in the equations below:

\[ \text{M} + \text{S}_2\text{H}_2\text{O} + \text{HS}^- + \text{H}_2\text{M(OH)}_2 \]  \hspace{1cm} (3)

\[ \text{P} + 2\text{H}_2\text{O} \rightarrow 1/2\text{H}_2 + \text{H}^+ + \text{H}_2\text{PO}_2^- \]  \hspace{1cm} (4)

Armijo (79) has measured the anodic polarization behavior of grain faces and grain boundaries in both a commercial and a high purity Fe-Ni-Cr alloy. No difference was detected between grain boundary and matrix behavior for the high purity alloy. However, when doped with 0.95% Si, a marked difference was found between matrix and grain boundary, the latter shown in dissolution rates an order of magnitude higher current densities over the entire potential range. Chuang, Lumsden, and Staehle (78) have obtained similar results with an Inconel 600 alloy.
<table>
<thead>
<tr>
<th>Alloy Studied</th>
<th>Segregating Species</th>
<th>Technique</th>
<th>Reference</th>
<th>Ref.#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 304 stainless steel (Solution annealed and quenched)</td>
<td>S,Ni,C (?)</td>
<td>AES</td>
<td>Joshi + Stein</td>
<td>42</td>
</tr>
<tr>
<td>Type 304 stainless steel (Solution annealed and aged for different times at 580 to 850°C)</td>
<td>S,Si,Ni,P,C (as carbide) + Cr depletion</td>
<td>AES</td>
<td>Joshi + Stein</td>
<td>42</td>
</tr>
<tr>
<td>Type 304 and 316 stainless steel</td>
<td>Mo (to free surfaces:)</td>
<td>AES</td>
<td>Bonnes, et al</td>
<td>81</td>
</tr>
<tr>
<td>18 CrNi Mill annealed steel</td>
<td>Mo</td>
<td>Chemical analysis of fracture surface</td>
<td>Ankharov</td>
<td>82</td>
</tr>
<tr>
<td>304L (cathodically charged)</td>
<td>H(?)</td>
<td>Intergranular mechanical embrittlement</td>
<td>Holsworth</td>
<td>83</td>
</tr>
<tr>
<td>Type 304 stainless steel (solution annealed and water quenched, slow cooled, sensitized)</td>
<td>S</td>
<td>AES</td>
<td>Chaung, Lumsden, + Staalhe</td>
<td>78</td>
</tr>
</tbody>
</table>

Table 1
They found increased dissolution rates when sulfur, boron, nitrogen, and carbon precipitation, and phosphorus had segregated to the grain boundaries.

Wilde and Greene (80) investigated the effect of impurities on the anodic polarization behavior of 38 different heats of Type 304 stainless steel (solution annealed) in 1NH₂SO₄. By means of a multiple correlation technique they found that the maximum current of the active dissolution peak, i.e., could be expressed by the following relationship:

\[ i_c = 15471 + 373(Mn) - 1240(Cu) - 750(mo) + 7600(S) - 6500(C) - 840(Cr) \]  

(5)

If those species having positive signs in the equation above were segregated at grain boundaries, increased dissolution during transient film rupture events would ensue and therefore increase susceptibility to IGSCC.

The work investigating the segregation of various minor alloying elements can be summarized as follows.

Various elements do segregate to grain boundary regions after heating. However, as the work of Chaung et al (78) shows, these species (in this case, sulfur) do not appear to be controlling the susceptibility to IGSCC. It is possible that the segregating species are contributing to IGSCC but the fact that quench annealed Type 304 stainless steel with sulfur segregated to the grain boundaries does not undergo IGSCC in high purity water is proof that the segregated sulfur is not determining the IGSCC susceptibility of the alloy.

2.1.7 Effect of Cold Work on SCC Susceptibility

When the constant extension rate test (CERT) is used as the basic method of determining an alloy's resistance to SCC, the amount of
extension, or cold work prior to crack initiation needs to be determined because the amount of cold work that a particular alloy has been subjected to influences its SCC susceptibility.

Cold work is a variable which can interact with the metallurgical state of the material and produce effects on the stress corrosion process not readily interpretable in terms of the gross strain. The strengthening effect of segregation or precipitation at grain boundaries may cause in one instance, with increasing strain, more severe dislocation pileups which are the critical event as far as stress corrosion is concerned (84). In another case, a general increase in dislocation density with increasing strain may result in a large number of competitive sites for solute impurities and hence, a decreased sensitivity of boundary regions to the corrosive environment. Or, cold-work and/or chromium depletion may induce partial martensitic transformation which in turn alters the corrosive behavior.

Early work by the USAEC (85) on bent beam samples showed cold working of annealed stainless steel without sensitization was in itself sufficient to cause stress corrosion in 316°C oxygenated water (1.6-3.1x10^-7 M O_2 (5 to 10 ppm O_2)). At a cold work level of 10%, intergranular cracking was found in Type 304 stainless steel. At the higher cold work levels the cracking became transgranular.

Clarke and Gordon (25) have confirmed annealed plus highly cold-worked material (30% uniform reduction) will fail transgranularly in 288°C oxygenated (3.1x10^-6 M O_2 (100 ppm O_2)) water at sustained stresses of 105% of the 288°C yield strength. However, these authors found no cracking at the 5, 10, and 20% levels after 950 hours of exposure.
Pickett and Sim (86) found no cracking in annealed plus cold worked Type 304 after 1000 hours in 288°C water containing 6.3x10^-6 M O_2 (200 ppb O_2) at fairly high sustained stresses.

Cowan and Gordon (49) report that the effect of cold work on increasing the susceptibility of austenitic stainless steels to stress corrosion is probably due to a combination of two effects. First, the cold working raised the yield stress considerably and allows the application of higher loads, especially with fixed deflection samples. Secondly, the cold working produces deformation-induced martensite.

Vermilyea and Indig (87) have shown that deformation-induced martensite in stainless steels leads to accelerated oxide film growth rate in high temperature water. This accelerated film growth should increase the kinetics of crack initiation and propagation if a film rupture mechanism of stress corrosion is operative.

2.2 Environmental Influences on Stress Corrosion Cracking

The environmental influences on stress corrosion cracking can be separated in the following manner: effect of temperature; effect of dissolved oxygen concentration; effect of potential; alloy dependencies; effect of chloride content; effect of solution pH; effects of stress, strain, and strain rate. Although the problem of IGSCC of sensitized stainless steel is a problem in many diverse industries, i.e. chemical, petroleum, automotive, agriculture, etc., the test environment selected for this study most closely resembles that found in boiling water reactors (BWR) and therefore this literature survey will concentrate on the environmental influences on SCC which are known to occur in high purity water.
Cracking has occurred in the weld sensitized areas of small diameter piping manufactured of Type 304 stainless steel. This cracking has occurred in the primary coolant systems of BWR's. These systems contain high purity water.

The chronology of SCC in BWR's due to sensitization of Type 304 stainless steel prior to 1976 is given below:

1955-1958 Several authors, including Scharfstein and Brindley (88), Williams (89), Edeleanu and Snowden (90), and Williams and Eckel (91), reported observing stress corrosion cracking of quenched stainless steels in high temperature water.

1965 First SCC in Dresden-1 plant adjacent to a weld in small diameter piping (92, 93, 94, 95).

1967 SCC in control rod drive stub tubes during construction of Tarapur and Oyster Creek plants (95, 96).

1970 SCC in the core spray safe end on the Nine Mile Point plant.

1974 SCC adjacent to weld in 4 inch bypass line around 18 inch value in main recirculation line of Mark 3 and Mark 4 BWR's (97,98).

1975 SCC adjacent to welds in 10 inch core spray lines in Mark 3 and Mark 4 BWR's (97,98).

The first stress corrosion crack in the Dresden-1 BWR plant occurred approximately 5 years after startup. Since that time more than 24 stress corrosion cracks have occurred in Dresden-1 (97). In most cases the cracks initiated on the I.D. of small diameter pipes, propagated intergranularly through the sensitized zone adjacent to the weld, and penetrated the O.D. surface to cause small leaks.
Although the case described in the preceding paragraph refers to cracking observed in a nuclear environment, the same mode of cracking, IGSCC in the heat affected zone of welds, is observed in many industrial applications where welded austenitic stainless steel is exposed to aqueous environments.

2.2.1 Effect of Temperature

There have not been any complete studies of the effect of temperature on the SCC of austenitic stainless steel in high purity water prior to this investigation. White, Berry, and Boyd (99) recently finished some work where they did look at the effect of temperature on SCC susceptibility. They elected to plot their data as shown in Figure 12. They have plotted the true fracture strength as % of inert as a function of the test temperature. Straight line relationships result. The true fracture strength values are obtained by dividing the fracture strength by the apparent final cross section of the specimen.

The general trend is the same as has been seen in the past; susceptibility to SCC increases as the test temperature increases. Pagodin, Senturev, and Bogayavlenkii (100) observed the effect of temperature.

White, Berry, and Boyd (99) also compared several other cracking indexes: true fracture stress, total energy input, the General Electric Index, and two Toshiba indexes (See Figure 13). These indexes are described in detail in Appendix A. The cracking indices do not provide any useful engineering information. The practice of reporting data in terms of an influence on crack growth rates should be used because useful design data can then be obtained.
Figure 12
Temperature versus true fracture strength at various dissolved oxygen ppm.

- 8.0 ppm
- 4.0 ppm
- 1.0 ppm
- 0.2 ppm
- 0.05 ppm
Figure 13
Comparison of cracking indexes. (99)
2.2.2 Effect of Dissolved Oxygen Concentration

It is impossible to discuss the effect of dissolved oxygen concentration on SCC without discussing the effect of the test temperature on the electrochemical potential of the sample. Therefore, only the general trends which have been observed are discussed in this section. Further discussion of this topic is included in Section 2.2.3.

Cheng (101, 94, 16) made some interesting and pertinent observations. Cheng states that dissolved oxygen in sufficient quantity may be desirable for carbon steel, but that it will release a high concentration of chromates in austenitic stainless steel and Inconel systems. This was confirmed by Berry (102). He found large amounts of chromium in the water as chromate after SCC tests of austenitic stainless steels in high purity water. Dissolved oxygen generally has little effect on the steady state corrosion rates of austenitic stainless steel and Inconel. However, the dissolved oxygen concentration has a marked effect on the solubility of the corrosion products and therefore affects the release of these products. Park, Agrawal, and Staehly (103) found that in caustic solutions, chromate ions form a redox couple CrO$_4^{--}$/CrO$_4^{--}$ which shifts the corrosion potential of the alloy into its passive region where there is high resistance to SCC. This indicates that crack initiation may occur by an oxygen reduction process yielding OH$^-$ but that crack propagation may involve a different mechanism since a local buildup of CrO$_4^{--}$ would tend to reduce the propensity for SCC.

The effects of oxygen concentration at 288°C on the susceptibility to cracking in an early study by White, Berry and Boyd (104) are shown in Figure 14. Using constant strain rate testing no cracking was
Effect of oxygenated water on SCC susceptibility\(^\text{(104)}\)
observed below $6.3 \times 10^{-6} \text{M } \text{O}_2 (200 \text{ ppb } \text{O}_2)$. 

More recent work by White, Berry and Boyd (99) considering the influence of dissolved oxygen concentration on SCC susceptibility is shown in Figure 15. In this study, SCC was observed at oxygen concentrations less than $6.3 \times 10^{-6} \text{M } \text{O}_2 (200 \text{ ppb } \text{O}_2)$ but the cracking mode had switched from IGSCC to TGSCC. Their observation of a cracking mode transition confirms observations of the transition mode during the research program upon which this dissertation is based.

All tests were conducted in a refreshed autoclave system. A Beckman Oxygen Analyzer was used to measure the dissolved oxygen concentration flow rate of approximately 50 cc/min, they report that no difference in oxygen concentration could be measured between the feed and the return water at any of the oxygen concentrations studied. ($6.3 \times 10^{-6}, 3.1 \times 10^{-5}, 3.1 \times 10^{-4}, 3.1 \times 10^{-3} \text{M}(2,1,10,100 \text{ppm})$. This is in opposition with the findings of General Electric and myself. At low oxygen concentrations in particular, with dissolved oxygen concentrations less than $25 \times 10^{-5} \text{M } \text{O}_2 (800 \text{ ppb } \text{O}_2)$, there is a large difference between the inlet and outlet concentration of dissolved oxygen. This difference becomes more important as the dissolved oxygen concentration of the inlet water decreases.

2.2.3 Effect of Electrochemical Potential

In beginning a discussion of the effects of the electrochemical potential on SCC susceptibility of a material the most logical point from which to begin the discussion is the potential-pH diagram which maps out the regions of stability for metals, oxides, gases, and dissolved species. This is a relatively easy task at room temperature
Figure 15  
True fracture strength versus dissolved oxygen at 400°F, 475°F, and 550°F (average value) (99)
since most of the needed thermodynamic data is readily available.
Pourbaix (105) describes the construction procedure and presents dia-
grams for the metal-water system in his Atlas of Electrochemical
Equilibria.

Many reactions of interest take place at elevated temperatures. 
Unfortunately most of the thermodynamic data needed to construct poten-
tial-pH diagrams at elevated temperatures does not exist. However, use
of the Entropy Correspondence Principle of Cross and Cobble (106, 107,
108) which relates the ionic entropies at room temperature to those at
high temperatures, enables one to make an estimate of the partial molal
head capacity. With this data the construction of the high temperature
potential-pH diagrams is now possible.

The diagrams pictured in Figures 16, 17, 18, 19, and 20 were con-
structed based on the Entropy Correspondence Principle (49, 109, 110,
111, 105). Only those reactions which were thought to be of the great-
est interest were included in the diagrams. Details of the construction
of the diagrams is presented in Appendix B.

Several general observations can be made from these diagrams with
respect to effect of temperature on the thermodynamic stability of the
various species:

(1) The range of stability (with respect to pH) of the oxide
phases in the acid region increases with increasing temperature.

(2) The range of stability (with respect to pH) of the oxide
phases in the basic region decreases substantially with increasing temp-
erature.

(3) The potential-pH range over which H₂O is stable decreases as
Figure 16 E-pH Fe-Cr-Ni, 100°C (119).
Figure 17 E-pH Fe-Cr-Ni, 150°C (119).
Figure 18  E–pH Fe–Cr–Ni, 200°C (119).
Figure 19  E-pH Fe-Cr-Ni, 250°C (119).
Figure 20  E-pH,Fe-Cr-Ni, 288°C (119)
the temperature increases.

(4) In the basic region the potential range in which water is stable shifts to lower potentials as the temperature is increased.

The extension of room temperature electrochemical techniques for the study of equilibrium and charge transfer processes in aqueous systems at elevated temperatures and pressures is now well established (112, 113). All electrochemical studies involve the measurement of the potential of an indicator ("working") electrode against a reference electrode (114). A major problem in all high temperature electrochemical studies in aqueous systems is choosing a suitable reference electrode. MacDonald (115) recently reviewed and assessed the various reference electrodes for high temperature aqueous systems. One of the best electrodes for use in high temperature-high purity water systems is the Ag/AgCl reference electrode. This electrode developed by Agrawal et al (116, 117) is described in more detail in Section 3.0.

There have been few electrochemical studies conducted on Type 304 stainless steel in high temperature, high purity water (118, 63, 49). Recently Lee (119) at the Ohio State University completed an extensive study of this system. In Figures 21 and 22 the potential-dissolved oxygen dependence of Type 304 stainless steel and platinum are shown respectively. At oxygen concentrations greater than $3.1 \times 10^{-6}$ mol (100 ppb) there is excellent agreement with Indig and McIlree (63). There is disagreement below $3.1 \times 10^{-6}$ mol $O_2$ (100 ppb $O_2$). The reason for this is unknown at this time. As expected, for a given oxygen concentration, an increase in temperature results in a decrease in potential on the surface of the specimen.
Figure 21
Corrosion potential vs. dissolved oxygen concentration - Type 304 stainless steel (119)
Figure 22
Corrosion potential vs. dissolved oxygen concentration - platinum (119)
Indig and McIlree (63) have also conducted some investigations into the high temperature electrochemical behavior of Type 304 stainless steel. The main conclusions of their study are:

(1) The resistance of welded Type 304 stainless steel to intergranular SCC as a straining electrode in .01N Na₂SO₄ at 275°C is dependent upon specific electrochemical potential, thermomechanical treatment, and composition.

(2) Anodic polarization studies at 288°C in .01N Na₂SO₄ performed with Fe-10Ni-XCr alloys (X 18) to simulate chromium depleted grain boundary material suggests that resistance to intergranular SCC decreases with increased potential because of increased anodic dissolution at low chromium content.

(3) A sigmoidal relationship exists between the potential of Type 304 stainless steel and dissolved oxygen in high purity water at 274°C. A significant increase in corrosion potential occurs with oxygen concentrations between 3.1x10⁻⁷ and 1.55x10⁻⁶M (10 and 50 ppb). (Figure 23).

(4) Potentials in .01N Na₂SO₄ at 274°C can be related to potentials in pure water by a .150V correction factor. The correction factor accounts for the change in high temperature pH due to hydrolysis.

Figures 24, 25, 26, and 27 show anodic polarization curves obtained by Lee (119) for quench annealed Type 304 stainless steel in high purity water at temperatures of 100, 150, 200, and 250°C. The most important aspects of these curves are:

(1) The presence of a transpassive peak.

(2) The transpassive peak shifts to lower potentials as the temperature increases.
Figure 23

Sigmoidal relationship between E and the dissolved oxygen content of the water (63)
Temperature: 100°C
Material: Quench Annealed Type 304 Stainless Steel
Solution: 0.1N Sodium Sulfate
Anodic Scan Rate: ~20 Minutes at Each Potential
Cathodic Scan Rate: 10 mV/20 Seconds

Figure 24
Polarization curve - Type 304 stainless steel, 0.1N sodium sulfate, 100°C (115)
Temperature: 150°C
Material: Quench Annealed Type 304 Stainless Steel
Solution: 0.1N Sodium Sulfate
Anodic Scan Rate: ~20 Minutes at Each Potential
Cathodic Scan Rate: 10 mV/20 Seconds

Figure 25
Polarization curve - Type 304 stainless steel, 0.1N sodium sulfate, 150°C (119)
Temperate: 200°C  
Material: Quench Annealed Type 304 Stainless Steel  
Solution: 0.1 N Sodium Sulfate  
Anodic Scan Rate: ~20 Minutes at Each Potential  
Cathodic Scan Rate: 10 mV/20 Seconds  

Figure 26  
Polarization curve, Type 304 stainless steel, 0.1N sodium sulfate, 200°C (115)
Temperature: 250°C
Material: Quench Annealed Type 304 Stainless Steel
Solution: 0.1N Sodium Sulfate
Anodic Scan Rate: ~20 Minutes at Each Potential
Cathodic Scan Rate: 10 mV/20 Seconds

Figure 27
Polarization curve, Type 304 stainless steel, 0.1N sodium sulfate, 250°C (11º)
Comparing Figures 27 and 28 illustrates the effect of sodium sulfate on the anodic kinetics of the system. The sodium sulfate is added to the solution to raise the conductivity enough to allow meaningful polarization experiments. However, as can be seen in Figures 27 and 28, the sodium sulfate additions are affecting anodic kinetics as well as the conductivity of the solution. Additions of sodium sulfate depress the corrosion potential (119). This result is in agreement with the work of Indig (120).

Indig and Vermilyea (70) investigated the corrosion of sensitized austenitic stainless steel in dilute acid at 289°C with electrochemical and corrosion techniques. They found that grain boundary crevices formed initially at the corrosion potential, but penetration was not significant because the crevices filled with corrosion product. Severe intergranular attack occurs if the sensitized alloy is polarized to a passive potential in a pH3 H2SO4 electrolyte. The general corrosion morphology changes significantly with potential. A thick layered oxide formed of the alloy was polarized at the peak of the active region while anodic protection was achieved in the passive region. Fe-Ni-Cr alloys, where the chromium content was less than 18%, were also used in the polarization and corrosion studies. The chromium composition of these alloys was similar to the local grain boundary compositions that might exist after a particular sensitizing treatment. The anodic polarization kinetics of these alloys depended upon solution pH and alloy chromium content. At pH 3 or less, alloys containing 12.5% chromium do not passivate. At small anodic polarizing potentials these alloys exhibit extremely high corrosion currents. Exposure of these alloys under open
Temperature: 250°C
Material: Quenched Annealed Type 304 Stainless Steel
Solution: 0.01N Sodium Sulfate
Anodic Scan Rate: ~20 Minutes at Each Potential
Cathodic Scan Rate: 10 mV/20 Seconds

Figure 28
Polarization curve, Type 304 stainless steel, 0.01N sodium sulfate, 250°C (119)
circuit conditions showed that corrosion increases with decreasing pH and chromium content. The corrosion rate of the alloys containing less than 12.5% chromium appeared to be limited by the diffusion of hydrogen ions to the corroding surface. The corrosion rate-limiting step of alloys containing greater than 12.5% chromium appears to be a chemical reaction at the metal-oxide interface involving activation. The importance of the slow film repassivation rate on the low chromium material cannot be emphasized enough because the chromium depleted zone adjacent to the grain boundaries after sensitization should behave in the same manner as the low-chromium material. The slow repassivation rate would allow dissolution of the material to occur following a film rupture event and therefore the possibility of SCC exists.

The polarization curves presented in Figures 29 and 30 show the effect of chromium on the electrochemical kinetics.

Figure 31 compares the polarization behavior of a sensitized and an annealed specimen of Type 302 stainless steel in pH 2.5 H₂SO₄.

The sensitized specimen shows a pronounced anodic peak when compared with the non-sensitized specimen.

Indig et al (63) also conducted a series of tests in order to determine the effect of temperature on various potentials of Type 304 stainless steel in high purity water containing .01N Na₂SO₄. The locations of the critical potentials investigated are indicated in Figure 32 and the results of the investigation are plotted in Figure 33. The onset of SCC can generally be associated with a film instability region on a polarization curve. Therefore by knowing the behavior of these instability regions as a function of temperature and dissolved oxygen
Figure 29
Polarization Curves - Effect of chromium on the electrochemical kinetics (70)
Figure 30

Effect of chromium content on the anodic polarization behavior of Fe-Cr-Ni alloys in deaerated water containing 0.1N Na$_2$SO$_4$ at 121°C (79)
Figure 31. Anodic polarization curves for annealed and sensitized austenitic stainless steel.
Figure 32
Schematic of the shape of the polarization curve for Type 304 stainless steel in high temperature water with the identification of several critical potential regions (63)
Figure 33

Effect of temperature on various potentials of Type 304 stainless steel in water with .01N Na$_2$SO$_4$. (63)
concentration, some predictions of the SCC susceptibility of the material can be made based upon the location of the potential of the specimen in relation to the location of the potentials denoting film instability (transpassive potential, active-passive potential, etc.).

Vermilyea and Indig (87) also obtained polarization curves using standard equipment and techniques in both static and refreshed systems. The results are shown in Figure 34.

The potential shift which is observed is due to uncertainty in the reference electrode. For the static case, iron oxidation almost entirely obscures the passive corrosion of the metal.

The general features of the passivation of stainless steel are clearly visible from the curve obtained in the pH 3 HgSO₄. At the open circuit potential stainless steel is "active"; upon polarization it becomes passive; at higher potentials the current increases presumably because of oxidation of Cr₂O₃ to chromate; secondary passivity then occurs; and finally oxygen evolution begins. The current in the region of secondary passivity falls to about the same level as in the passive region— the current being determined by oxidation of Fe⁺² and not by corrosion of the metal, which proceeds at a much slower pace.

Many aqueous corrosion processes of technical interest occur under conditions where the access of electrolyte is restricted. These cases, where corrosion occurs under conditions of restricted diffusion, have been classified by Brown under the term "occluded cell corrosion (OCC)" (121).

A complete discussion of the localized corrosion process is given by Pourbaix. An excerpt is given below (121):
Polarization curves for Type 304 stainless steel on pH 3 \( \text{H}_2\text{SO}_4 \) in static and refreshed autoclaves\(^\text{(*)}\)
"In cases where the corroding solution contains oxygen, the surfaces which are outside the occluded cavities and in direct contact with this solution, are often passivated by oxygen, and are acting as aerated cathodes where oxygen is being reduced to water and/or to hydrogen peroxide with increase of pH.

The surfaces which are inside the occluded cavities are active and are acting as nonaerated anodes, where the metal undergoes corrosion and hydrolyzes with decrease of pH. This leads (when the corroding solution is a somewhat neutral aerated water) to cells of differential aeration between large passive cathodes where the solution is slightly alkaline and small active anodes where the solution is distinctly acid. The coupling of these cathodic and anodic reactions involves a transfer of anions from the external cathodes to the internal anodes so that the electroneutrality of the solutions inside both compartments may be secured."

Although it appears that an occluded cell could be operating, it is doubtful because if it were operating, pitting would probably be observed. There has been no evidence of pitting occurring on Type 304 stainless steel in high purity water. I do, however, think that there is some oxygen starvation occurring at the tips of the stress corrosion cracks. The difference in oxygen concentrations between the bulk concentration and that at the crack tip is not great enough to categorize the process as an "occluded cell".

Cowan and Kaznoff (122) and Indig (120) have performed a series of electrochemical tests in operating boiling water reactors (BWR). The primary object of the studies was to measure in-reactor phenomena and
### Table 3 Comparison of Sensitization Treatment 24 Hours at 1150 °F Versus 28 Hours at 932 °F

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Sensitized 9/1/7
Sensitized 11/30/7

(99)
to characterize in-reactor environmental variables so that out-of-reactor corrosion tests can be made more meaningful.

Cowan and Kaznoff (122) obtained some very important electrochemical data from the Dresden I nuclear reactor. The data was obtained in the inlet piping of a steam generator through the use of a blind flange attached to the piping. In Figure 35 the water temperature and the corrosion potential of a Type 304 and Pt are plotted as a function of time. The strong dependence of the corrosion potentials on the temperature of the water is clearly evident.

similar data that has been obtained by Indig (120) from the Vermont Yankee Nuclear Power Station.

The values for the open circuit potentials obtained in this study are in agreement with those obtained in laboratory studies at the Ohio State University and General Electric. By studying the potential-time behavior of various reactor components, it is hoped that certain "dangerous" potential regions can be avoided or at least the time spent within such regions minimized.

2.2.4 Alloy Dependence

Various alloys possessing a variety of heat treatment can behave differently when exposed to the same test mediums. The results reported in this section refer to alloys of the Fe-Cr-Ni alloy system. Additional information concerning the effects of various alloying additions on SCC resistance is included in Section 2.1.1 and 2.1.2.

Vermilyea (123) studied the SCC of iron and nickel base alloys in aqueous sulfate solutions at 289°C using a straining electrode apparatus. He found that the cracking susceptibility decreased in the order:
Figure 35
Water temperature and corrosion potential versus time - Dresden I BWR (127)
sensitized stainless steel, cold worked stainless steel containing martensite, sensitized Inconel 600, annealed stainless steel, and annealed or cold worked Incanel 600 and alloy AL 326. High cracking susceptibility usually occurs when conditions result in the development of thick reaction products. Acid conditions and chromium depletion favor thick reaction products and therefore enhance susceptibility.

Table 2 lists the effects of the degree of sensitization on the SCC behavior of Types 304 and 316 stainless steel in oxygenated BWR water. The degree of sensitization of the material does not exert a strong influence on SCC susceptibility according to this investigation.

White, Berry, and Boyd (99) also made a comparison of sensitizing treatments in their study (See Table 3). The data shows that a higher sensitizing temperature produces a slightly higher susceptibility to SCC in the range of 204°C to 260°C in 2.5x10^-4 M O_2(8ppm O_2) water.

In Table 4 the effects of various heat treatment on the SCC behavior of 304 stainless steel in BWR water with 3.1x10^-3 M (100 ppm O_2) are compared. No detrimental effect was produced by the homogenizing treatments.

In general, the 304 stainless steel alloy appeared to be slightly more resistant to SCC than the 316 alloy.

The most recent data showing the effect of the degree of sensitization on IGSCC susceptibility (See Figure 10) indicates that as the degree of sensitization increases (measured with EPR test) the susceptibility to IGSCC also increases. This area concerned with the effects of metallurgical structure on SCC resistance is an area requiring a great deal of work in order for accurate predictions of IGSCC resistance based
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Type 304 Stainless Steel (Both Hours)

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Type 316 Stainless Steel

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**Sensitized 932°F**

**Sensitized 1150°F**
TABLE 4 — Effect of Various Heat Treatments on the Stress Corrosion Cracking Behavior of Type 304 Stainless Steel in BWR Water with 100 ppm Oxygen

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Surface Finish</th>
<th>Failure Time (1)</th>
<th>No. of Failures/No. of Tests</th>
<th>Longest Exposure Time Without Failure, days</th>
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</thead>
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<td></td>
<td></td>
<td>2Sm</td>
<td>3Sm</td>
<td>2Sm</td>
</tr>
<tr>
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<td>Abraded</td>
<td>N</td>
<td>N</td>
<td>0/1</td>
</tr>
<tr>
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<td>Abraded</td>
<td>—</td>
<td>N</td>
<td>—</td>
</tr>
<tr>
<td>Heavily sensitized, homogenized, furnace cool</td>
<td>Abraded</td>
<td>N</td>
<td>N</td>
<td>0/1</td>
</tr>
<tr>
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<td>Abraded</td>
<td>—</td>
<td>N</td>
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</tr>
<tr>
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<td>Abraded</td>
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</tr>
<tr>
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<td>—</td>
<td>N</td>
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</tr>
<tr>
<td>Homogenized, furnace cool, not sensitized</td>
<td>Abraded</td>
<td>—</td>
<td>N</td>
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</tr>
</tbody>
</table>

(1) N = no failure, and blank indicates no test conducted.
upon sensitization tests alone to be made.

2.2.5 Effect of Solution pH

It is well known that the pH of the test medium has a strong influence on corrosion reactions. Since dissolved oxygen is present in the high purity water used in the tests, any reduction of this oxygen would yield a localized increase in the pH of the solution. Therefore, stress corrosion experiments which have been conducted in caustic solutions are discussed in this section.

Caustic SCC experiments were conducted on Type 304, 304L, 316, 316L, and USS 18-18-2 stainless steels by Wilson, Pement, and Aspden (124). The environments used were deoxygenated 50% NaOH solution at 316 and 371°C, deoxygenated 10% NaOH solution at 316°C, and atmospheric boiling (149°C) 50% NaOH. Variations in crack morphology were observed with caustic concentration and alloy content. The failures of Type 304 and 304L stainless steels in 50% NaOH solutions at 149, 316, and 371°C are transgranular. Increasing the temperature reduces the time to failure. In 10% NaOH solution at 316°C, the failures in Type 304 and 304L stainless steels are intergranular. All Type 316 and 316L stainless steels failed transgranularly in 50% NaOH at 149, 316, and 371°C and in 10% NaOH at 316°C. The similarity in the behavior of Type 304 and 304L steels and 316 and 316L steels indicates that carbon content has little effect on cracking susceptibility. Grain boundary carbides, per se, do not induce susceptibility to intergranular SCC in Type 304, 304L, 316L, and USS 18-18-2 steels.

Cels (125) has also observed intergranular SCC of Type 304 stainless steel in 10% NaOH at 288°C.
Chittenden and Hoveke (126) found a lower corrosion rate in pH 8.5-9.5 ammoniated water. Similarly, Rockwell and Cohen (127) reported that the yield of transportable corrosion products in an in-pile stainless steel system was much lower at pH 10-11 than with neutral solution.

Agrawal et al (128) investigated the polarization behavior of Fe-Ni-Cr alloys in concentrated sodium hydroxide solutions in the temperature range 25° to 150°C. Iron and nickel, as well as the Fe-Ni-Cr alloys, showed an active-passive transition which correlates well with the predictions of the pourbaix diagram both with respect to $M/\text{HMO}_2^-$ dissolution and oxide formation. Chromium on the other hand exhibited a transpassive Tafel behavior with an inflection corresponding to the $\text{CrO}_3^{-3}/\text{CrO}_4^{-2}$ equilibrium. The hydrogen evolution reaction and oxygen evolution reaction follow generally predicted behavior. The corrosion rates increased with an increase in the temperature and NaOH concentration. In the NaOH environment nickel is the most corrosion resistant and desirable component in the Fe-Ni-Cr alloys, whereas chromium is generally deleterious.

Berge et al (129) compared the SCC behavior of Type 316 stainless steel, Incoloy Alloy 800, and Inconel 600 in caustic solutions. The effects of sodium hydroxide solution concentration, stress level, and material structure and composition were among the variables investigated. They conclude that:

(1) Under high stresses and for concentrated solutions, stainless steel is much more susceptible than Alloy 600. However, below a threshold stress, which depends on the concentration of the solution, stainless steel is no longer susceptible whereas no such threshold has been
found for Alloy 600. This leads to a reversal of the classification of the alloys when the stress and/or the caustic concentration decreases.

(2) The small influence of sodium hydroxide concentration on the cracking of Alloy 600 leads to the hypothesis that the cracking in pure water, to which this material is susceptible, could be the same phenomenon as caustic cracking extrapolated to low sodium concentrations.

Theus (130) also observed IGSCC of Inconel 600 in 10% sodium hydroxide at 288°C.

Armijo (131) observed that cracking in pH 10 water occurred only in double U-bend specimens which contained crevices and not on single U-bend specimens. The local pH in the crevice could be significantly lower than the bulk solution. Copson and Economy (132) obtained similar results. They observed IGSCC in pH 10 NH₄OH and pH 10 LiOH; however, the cracking that occurred in pH 4 H₂SO₄ was more severe. Neumann and Griess (133) did not observe a pH effect on the SCC resistance of Type 347 stainless steel in high temperature water.

It is difficult to draw conclusions on the effect of pH on the SCC of austenitic stainless steels since no complete testing program investigating the effect has been conducted. However, the following conclusions are drawn:

(1) IGSCC of Type 304 stainless steel occurs in 10% NaOH at temperatures in excess of 288°C.

(2) TGSCC of Type 304 stainless steel occurs in 50% NaOH at temperatures in excess of 288°C.

(3) IGSCC of Type 304 stainless steel occurs in high temperature pH 4 H₂SO₄.
(4) In high temperature water an increase in pH leads to a reduction in the IGSCC propensity for cracking.

Several authors have investigated the effects of chromate and nitrate additions on the susceptibility of Type 304 stainless steel to cracking in high temperature water.

Park, Agrawal, and Staehle (103) investigated the effect of sodium salts on the SCC behavior of Type 304 stainless steel in boiling 20N NaOH. Of the sixteen additives tested, only Na$_2$CrO$_4$ was found to be effective in inhibiting SCC of Type 304 stainless steel in the caustic solution. The CrO$_4^{--}$ ions in caustic solution form a redox couple CrO$_4^{--}$/CrO$_3^{--}$, which shifts the corrosion potential of the alloy into its passive region where there is high resistance to SCC.

Scharfstein and Brindly (88) and Neumann and Griess (133) have both shown that addition of chromate ions inhibits the chloride stress corrosion cracking of austenitic stainless steels. The effect is thought to be due to a shift in the pH of the solution to higher values where the material is not susceptible to cracking.

Phillips and Singley (134) have shown that sodium nitrate inhibits the chloride stress corrosion attack of Type 347 stainless steel in tilting autoclave tests if the mole ratio of nitrate to chloride used is at least unity and the pH of the solution containing chloride is higher than about 10.5.

Lee (119) recently completed a study of the effect of chromate and nitrate additions on the corrosion potential of several Fe-Ni-Cr alloys and platinum at 250°C. Chromate additions increased the potential of the alloys as much as 600 mV. Increasing the chromate concentration
slightly decreased the potential of the alloys, possibly due to the change in pH. Nitrate additions of $1.6 \times 10^{-5}$ to $4 \times 10^{-4}$ M (1 to 25 ppm) did not affect the corrosion potentials of the alloys.

The results obtained in this study indicate that IGSCC occurs when the potential of the alloy lies in the transpassive region corresponding to valence change of the chromium ion. Since chromate additions place the potential of the alloy in this range the possibility of cracking exists.

Transgranular SCC has been observed at the potentials observed for the specimens in the solutions containing nitrate. However, this cracking does not initiate unless stresses well above yield are applied.

### 2.2.6 Effect of Chloride Content

An investigation into the effect of chloride ions on the SCC susceptibility of Type 304 stainless steel in high purity high temperature water has been carried out by Hishida and Nakada (135, 136). Chloride ions promoted stress corrosion cracking of both annealed and sensitized Type 304 stainless steel in high temperature water containing high dissolved oxygen at 286°C. It was found that chloride concentrations of $5.6 \times 10^{-6}$ or $2.8 \times 10^{-5}$ M (.2 or 1 ppm) caused intergranular cracking of the slightly sensitized steel in high temperature water containing high dissolved oxygen. However, in high temperature water containing low dissolved oxygen, chloride ion additions up to $2.8 \times 10^{-5}$ M (100 ppm) did not influence SCC behavior of Type 304 stainless steel.

Load elongation curves are presented in Figures 38, 39, and 40. Figure 38 is for annealed material, Figure 39 for slightly sensitized material, and Figure 40 for heavily sensitized material. The effect of
Figure 38
Stress - Elongation curves of annealed Type 304 stainless steel from constant strain rate tests conducted in undeerated water with varying chloride ion concentration (135, 136)
Figure 39
Stress - Elongation curves of slightly sensitized Type 304 stainless steel obtained from constant strain rate tests conducted in undeaerated high temperature water with varying chloride ion concentrations (135, 136)
Figure 40
Stress - Elongation curves of sensitized Type 304 stainless steel obtained from constant strain rate tests conducted in undeeaerated high temperature water with varying chloride ion concentrations (135, 136)
the chloride ion becomes more pronounced as the degree of sensitization of the material increases.

Observations of the fracture surfaces by SEM showed that SCC occurred transgranularly in annealed Type 304 stainless steel and intergranularly on sensitized Type 304 stainless steel (650°C, 2 hr.). However, the fracture mode of slightly sensitized Type 304 stainless steel (650°C, 1/4 hr.) changed from transgranular cracking to intergranular cracking as the chloride ion concentration was increased in the water containing high dissolved oxygen.

Scharfstein and Brindly (88) observed chloride SCC in cold worked and stresses austenitic stainless steels after exposure to water containing as little as 1.4x10^{-4}M (5 ppm) chloride at temperatures as low as 74°C to 93°C. The sensitized austenitic stainless steel cracks predominantly intergranularly. Unsensitized material cracked transgranularly.

2.2.7 Effect of Stress, Strain, and Strain Rate on SCC

Irrespective of whether the specimen is smooth or contains a pre-crack, the method of stressing the test specimen involves either:

(a) a constant total strain;
(b) a constant load; or
(c) a constant extension rate.

Constant total strain tests form by far the most popular type of test as a group since bend tests, in a variety of forms and usually employing simple, cheap, restmining jigs, come into this category. The problems of such test methods are usually related to poor reproducibility of stress level, if indeed any quantitative measure of the latter is
available. Parkins et al (137) have prepared an excellent report which discusses the various methods of SCC testing.

In constant load tests the cross section of the test piece is reduced by crack propagation. Therefore constant load tests involve an increasing stress situation. Consequently these tests are more likely to lead to early failure or total failure than constant strain tests.

Constant extension rate tests (CERT) involve the pulling of specimens to failure at a slow strain rate. Actually in constant total strain and constant load tests, crack propagation occurs also under conditions of slow dynamic strain to a greater or lesser extent depending upon the initial value of stress in relation to the effective yield stress of the test piece. Constant extension rate tests are positive in that they invariably produce fracture, either by stress corrosion or by some other mechanism and this occurs in a relatively short period of time. The constant extension rate test is considered a relatively severe type of test because it frequently promotes stress corrosion failure in the laboratory where other tests on smooth specimens do not promote cracking.

The constant extension rate test was chosen as the test technique to be used for this investigation primarily due to the positive nature of the test technique and the rapidity with which the tests could be conducted. Use of this technique would allow rapid screening of materials subjected to the various environments of concern in the shortest amount of time.

As mentioned in the previous section, the CERT test is generally considered to be a rather rapid, severe, SCC test used primarily for
sorting materials for use in SCC environments. As stated by Parkins (138), "In recent years understanding of the implications of slow dynamic strain testing has developed and it now appears that this type of test may have much more relevance than just that of an effective, rapid, sorting test".

Murata and Staehle (139) developed a theory of the straining film covered electrode. Other quantitative analysis of straining electrodes have been made by Gutman (140, 141), Eyring et al (142), Bockris et al (143), Windfeldt (144, 145), and Devanathan and Fernando (146).

The method of assessing the results where SCC is observed can be by a variety of parameters (147, 148, 99, 149). The effects of SCC are reflected in the load-deflection curve that may be recorded during a strain rate test and, since stress corrosion failure is usually associated with relatively little macroscopic plastic deformation curing crack propagation, a comparison of the load-deflection curves for specimens with and without SCC will usually reveal marked differences. Additional means of comparing results involve the elongation to fracture, time to failure, maximum stress, fracture stress, true fracture stress, crack propagation rate, and reduction in area. In some cases combinations of the mechanical properties can provide greater distinction between conditions of varying cracking severity. Further discussion of the various methods used for analyzing the data obtained in CERT tests is provided in section 4.

The CERT test is a severe test and it is possible to produce results that do not show good correlation between the cracking propensities determined in CERT and other methods of testing. Such results may
in fact be no more than a demonstration of the importance of strain rate, as opposed to stress per se, in real situations, and this together with the reasonable correlation from tests where positive results are given by both methods of testing being compared, suggest that the strain rate may be significant in its own right. The relevance of strain rate effects in static load tests with their overtones for non-propagating cracks, the concept of an electrochemically dependent range of strain rates within which SCC occurs and the significance of load cycling in sustaining creep and hence cracking, all support this conclusion (168).

In Parkins (138) arguments there are numerous references to the importance of a critical creep rate or strain rate at the crack tip. This creep can account for the repeated plastic deformation that is needed at the crack tip in order for SCC to continue. The argument is essentially the same as that pursued by Vermilyea (150). This approach involves the following steps (13):

(1) The passive film ruptures.
(2) The metal corrodes until repassivation is complete.
(3) Creep continues at the crack tip. Because of the relatively low temperatures at which SCC occurs, the creep process was considered to be transient, and this has been confirmed by Petit and Desjardins (151),
(4) At a critical strain, the passive film ruptures, and the cycle is repeated,

In this model rather than invoking slip step emergence as a requirement for film rupture, the film is thought to remain intact and fully protective during step 3 while the substrate undergoes plastic
deformation, film rupture occurring at some macroscopic strain. Such a
model would not appear to attach particular significance to the occur-
rence of coplanar slip, except perhaps for its influence on the creep
rate.

For thin passive films on stainless steels exhibiting coplanar
slip, it would appear more likely that film rupture would result di-
rectly from slip step emergence during creep (13). The crack tip could
be imagined to encounter a flux of dislocations on a series of active
slip plans. Pugh (13) describes some interesting possibilities from
this point:

"The creep rate at the crack tip would be strongly dependent on
the magnitude of the local stress, so that this offers a rationale for
the commonly observed relationship between the rate of cracking and the
stress intensity. Thus at small creep rates when the number of film
rupture events per second is small, the case could be envisaged where
repassivation is complete after every event and the rate of cracking is
determined by the creep rate and hence the stress intensity (correspond-
ing to region I, da/dt vs. stress intensity). At large creep rates, on
the other hand, the rate of film rupture could be so rapid that the
crack tip is effectively film free at all times, so that the rate of
cracking is independent of the creep rate (region II), being controlled
entirely by the rate of anodic dissolution. The activation energies for
regions I and II would then be expected to correspond to those for tran-
sient creep and anodic dissolution, respectively."

Diegle and Boyd (152) state that the success of the slow strain rate
technique in producing SCC in laboratory investigations results from
the film covered nature of alloys in corrosants which cause SCC. It is proposed that the rate of strain is either to promote repetitive film rupture, or possibly to maintain (through enhanced dissolution) a transition film of poor protective quality, which in turn facilitates crack initiation and propagation by a particular mechanism.

Solomon, Povich, and Devine (153) investigated the effect of strain rate on the SCC of an austenitic stainless steel in MgCl₂ solutions. Crack propagation mode (intergranular vs. transgranular) was a function of strain rate and temperature. At low strain rates, the rate determining step of the SCC corresponded to the formation of slip steps, but at higher strain rates, the rate determining step appeared to be a corrosion process on the slip steps. SCC was most prevalent when the formation rate of the slip steps was equal to the corrosion rate of the steps (154).

Scully (155) points out that the application of constant strain-rate conditions to the study of stress corrosion crack propagation is a logical development in the study of stress corrosion mechanisms. It focuses attention upon the rate of plastic deformation occurring at the tip of a propagating crack. The rate at which this plastic deformation occurs constitutes the principle mechanical factor in crack propagation.

Hishida, Nakada, and Ito (156) conducted a series of tests using the constant extension rate test to determine the effects of strain rate and degree of sensitization on the susceptibility to cracking of Type 304 stainless steel in high temperature water. The effect of strain rate on elongation to fracture is shown in Figure 41. Lower strain rates yield lower elongations given the same environmental conditions.

Figure 42 illustrates the effect that oxygenated water has on sensitized Type 304 stainless steel. IGSCC is observed in oxygenated
Figure 41
Crosshead speed (mm/min)
Dependence of elongation to fracture on strain rate (156)
Stress-elongation curves in various conditions.

Crosshead speed: 0.01 mm/min
(Strain rate: $5 \times 10^{-4}$ mm/min/min)

Figure 42 Effect of oxygenated water on elongation to fracture (156)
Hanneman (157) has recently reported that surface preparation of the sample does effect the outcome of constant extension rate tests. It had been assumed prior to this work that crack initiation events were not influenced by the surface conditions of the specimen when the specimen was tested in CERT. Obviously the magnitude of this influence needs to be determined more accurately.

The desire to obtain meaningful design data from stress corrosion tests along with the desire to more accurately define the stress state of sample was responsible for the introduction of fracture mechanics concepts to stress corrosion research.

The fracture mechanics approach to SCC has evolved over the last fifteen years. The linear fracture mechanics formalism was first applied to the study of stress corrosion crack growth by Brown and Beachen (158) and Johnson and Willner (159). In essence, the approach recognizes the presence or early initiation of cracks in a structural component, and that structural failure results from the growth of these cracks by SCC. The mechanical driving force for this crack growth is considered to be given by the crack. Tip stress intensity factor (K_I) is defined by linear elasticity (160).

The most common method used in fracture mechanics based experiments involves the measurement of the time-to-failure for precracked specimens under different applied loads, and the determination of a so-called threshold K_{ISC}, below which presumably no failure can occur as a result of SCC. The level of K_{ISC} in relation to K_{IC}, the plane strain fracture toughness of the material, gives a measure of its SCC
susceptibility and is often used in materials selection and design (160).

The existence of a K-independent stage (Stage II) of crack growth suggests that crack growth in this stage is rate limited by the operative chemical process for SCC (160). This provides the essential link between the mechanical and chemical aspects of SCC, and represents a most important contribution of linear fracture mechanics. By examining the responses of Stage II growth rates as functions of temperature and pressure, or concentration of corrosive species, and comparing them to those for candidate chemical processes, it is possible, at least in principle, to deduce the rate controlling processes and mechanisms for SCC.

The crack growth rates reported in this investigation are Stage II crack growth rates. This was determined by conducting experiments at various strain rates while maintaining the test environment constant. The crack growth rates did not vary significantly as a function of strain rate. The strain rate can be related to the stress intensity at the crack tip and it can therefore be concluded that at the strain rates employed for this investigation, Stage II crack growth is occurring.

Workers at Battelle reported the crack growth data shown in Figure 43 (104). The depth of the cracked region on an SEM photograph of the fracture surface was measured and the value obtained was then divided by the total time for the test. This results in an apparent crack propagation rate. It does not account for the initiation portion of the total measured failure time or for the change in stress as the crack propagates.
Figure 43. Apparent IGSCC propagation rate of AISI Type 304 stainless steel in 288°C water (1.2 x 10^-3 M O₂) (36ppm) as determined by SEM measurements (104)
For many materials, including Type 304 stainless steel, the linear elastic analysis used to calculate $K_{IC}$ is invalidated by the formation of large plastic zones and elastic-plastic behavior. Therefore considerable effort has been devoted to the development of elastic-plastic fracture-mechanics analysis as an extension of the linear-plastic analysis.

Two of the most promising extensions of linear-elastic fracture mechanics into the elastic-plastic region are the following:

1. Crack-opening displacement (COD);
2. $J$ integral.

Of these methods I would like to focus my attention on the path independent $J$ integral approach proposed by Rice (161). The $J$ integral approach is a method of characterizing the stress-strain field at the tip of a crack by an integration path taken sufficiently far from the crack tip to be substituted for a path close to the crack tip region. Even though considerable yielding occurs in the vicinity of the crack tip, if the region away from the crack tip can be analyzed, behavior of the crack-tip region can be inferred.

For linear-elastic behavior, the $J$ integral is identical to $G$, the energy release rate per unit crack extension. Therefore a $J$ failure criterion for the linear-elastic case is identical to the $K_{IC}$ failure criterion (162). For linear-elastic plane strain conditions,

$$J_{IC} = G_{IC} = \frac{(1-\nu^2)(K_{IC})^2}{E}$$

(6)

The energy line integral, $J$, is defined for either elastic or elastic-plastic behavior as follows:
\[ J = \int_R \frac{W dx}{\frac{S}{dx}} \]  

where \( R \) = any contour surrounding the crack tip;

\( W \) = the strain energy density = \( \int_0^\infty \sigma \, d\varepsilon \);

\( T \) = the traction vector defined according to the outward normal \( n \) along \( R \), \( T_i = \sigma_{ij} n_j \);

\( U \) = Displacement vector;

\( S \) = arc length along \( R \).

For any linear-elastic or elastic-plastic material treated by deformation theory of plasticity, Rice (163) has proven path independence of the \( J \) integral.

Considerable work on developing the \( J \) integral as an analytical tool for elastic-plastic crack-tip field analysis has been performed by Begley and Landis (164, 165) using a compliance technique.

Although this technique for measuring \( J \) appears to give reasonable results, methods for measuring \( J \) from a single specimen design would be much more desirable, and such methods were developed by Bucci et al (166) as well as by Rice et al (167).

The methods developed by Rice et al (167) for measuring \( J \) on deeply notched, bend-type specimens appeared to offer the simplest single specimen design technique for measuring \( J \) and was further developed by Landis and Begley (168). Summarizing the procedure for \( J \) measurement:

(a) Load specimens to various displacements; (b) Calculate \( J \) for each specimen and plot versus \( a \); (d) Construct the line \( J = 20_{\text{flow}} \, a \) and the line \( J \) versus crack extension; and (e) Mark \( J_{\text{IC}} \) at the intersection of the lines constructed in (d).
For the tests conducted in this investigation the amount of deformation prior to crack initiation invalidates the J-integral approach. If crack initiation occurs prior to 5% plastic deformation application of the J-integral approach would be valid. This would allow the calculation of a $J_{ISC}$ for the material in the test environment.

An area which was outside the scope of this investigation but which is of extreme importance is the effect of cyclic loading on the SCC resistance of austenitic stainless steels in high purity water environments.

Nagashima (169) investigated the environment-enhanced crack propagation of sensitized Type 304 stainless steel under cyclic loading in oxygenated high temperature water. The stress level and water chemistry were fixed during the test, and the effect of load wave form was made a variable. The following observations were made:

1. Exposure to a simulated BWR environment accelerated the crack growth rate of sensitized stainless steel compared to ambient air.
2. The loading frequency played an important role in influencing the crack growth behavior of sensitized stainless steel. The lower the loading frequency, the higher the cycle-dependent crack growth rate.
3. At loading frequencies below about 20 cycles/min., coexistence of intergranular SCC and transgranular corrosion fatigue cracking was observed in oxygenated water.
4. Based on the superposition model proposed by Wei and Landes (170), the calculated SCC growth rate at a stress intensity factor of $30.0 \text{ MN m}^{-3/2}$ in oxygenated $200^\circ\text{C}$ water was $6.7 \times 10^{-6} \text{ mm/sec}$. 
The problem of corrosion fatigue in the austenitic stainless steel-high purity water system has only recently begun to be investigated. Work by Parkins and others has shown that the superposition of a cyclic load on a high mean stress can lead to accelerated cracking of materials. Research activities in this area should be intensified.

2.2.8 Summary of the Environmental Influences on SCC - Literature

A summary of the environmental influences on the stress corrosion cracking of austenitic stainless steel which are relevant to the present investigation is listed below:

1. The effects of dissolved corrosion products and solution pH must be determined before the IGSCC of austenitic stainless steel in oxygenated high temperature water can be understood (46).

2. Stressed Type 304 stainless steel exhibits IGSCC in high purity water containing more than $3.1 \times 10^{-6} \text{M O}_2 (100 \text{ ppb O}_2)$ at $288^\circ \text{C}$.

3. Crevices are not necessary for IGSCC to occur in sensitized alloys (46).

4. The induction time or nucleation time for cracking of sensitized Type 304 stainless steel in oxygenated water at $289^\circ \text{C}$ increases markedly when the applied stress is decreased from $207 \text{MN/mm}^2 (30 \text{ksi})$ to $138 \text{MN/mm}^2 (20 \text{ksi})$ (171).

5. Sensitizing treatments of 7 or 24 hours at $621^\circ \text{C}$ produce a high degree of susceptibility to SCC in Type 304 stainless steel (104).

6. Sensitized wrought 304, 309, and 316 stainless steels appear to be about equally sensitive to SCC in high temperature oxygenated water (104).
(7) Type 304L, stabilized 347, 308L weld deposit, Incoloy 800, and Inconel 600 that have been "sensitized" at 621°C are resistant to SCC under the same conditions that produce cracking in sensitized 304, 309, and 316 stainless steels (104).

(8) The IGSCC of sensitized austenitic stainless steels decreases with decreasing temperature (100).

(9) The cracking process appears to occur by a mechanoelectrochemical process (46).

(10) Cracking appears to nucleate in plastically deformed areas on the surface (46).

(11) Cathodic protection apparently eliminates crack nucleation (46).

(12) Transgranular stress corrosion cracking TGSCC has been observed on Type 304 stainless steel in deaerated water, $1.8 \times 10^{-6}$ M (60 ppb $O_2$) at 288°C (99).

(13) An apparent greater susceptibility to IGSCC exists in $1.25 \times 10^{-4}$ M $O_2$ (4 ppm $O_2$) water than in $2.5 \times 10^{-6}$ M $O_2$ (8 ppm) (99).

The data obtained in this investigation os compared with the existing data in Section 4.0. Any agreement or disagreement with existing ideas is presented in Section 4.0.

2.3 Microprocesses of Stress Corrosion Cracking

Mechanistic hypotheses use models for embodying principal concepts. Staehle (20) has outlined and criticized various models which have been proposed to describe the stress corrosion cracking process.

The simplest idea for the advance of cracks arises from the Griffith
idea of bond breaking to form new surfaces. Adsorption of various ions at the crack tip supposedly lowers the surface energy which leads to a decreased bond strength at the crack tip. Uhlig (172), Coleman et al (173) and others have proposed that this concept be applied to interpreting stress corrosion cracking in aqueous environments. Weakened and stressed metal bonds combined with a critical environmental species leads to advancement of the crack. The primary argument against this model is that crack advance is clearly an electrochemical dissolution process and therefore does not depend upon the adsorption of any particular chemical species.

Models incorporating the effects of film repassivation kinetics in their ideas have become the most popular models. Starting with an instantaneously clean surface arising from slip, a metal in a nominally filmed condition will react to form a new protective layer. The rate of formation of this new layer, as for the step recession argument, determines whether or not a high 1/d geometry can develop. If the rate of reformation of the film is too rapid, then negligible penetration occurs; and if the rate of re-formation is too slow, the surface dissolves. Only at intermediate rates of repassivation will localized attack develop. Logan (174,175) origanally suggested the film rupture theory of SCC. The theory is based upon the successive breaking and reformation of a passive film (See Figure 44).

Work by investigators such as Swann (176, 177), Swann and Embury (178), Smith and Staehle (179), and Staehle (33), and others have advanced the evolution of the slip dissolution theory to its present status. The film rupture idea in its simplest form has been outlined in detail
Figure 44

Schematic figure illustrating relationship between current versus time transient, and amount of material dissolved for given slip step event.

Case I - rapid repassivation
Case II - intermediate repassivation - favors stress corrosion cracking
Case III - extensive or non-restricted lateral dissolution (20)
by Smith and Staehle (179) and Staehle (180). Generally when slip is
discrete, the film is easily broken cleanly; when slip is less coplanar,
the film retains some of its continuity (181).

The breaking and reformation of films appears to be associated with
two processes:

1. An amount of metal dissolves.
2. The film reforms after a particular period of time.

The amount of material which is irretrievably lost amounts to the
incremental advance of chemical penetration, or cracking.

Forty and Humble (182,183) were the first to introduce an alternative
interpretation of the film rupture idea. This idea was incorpo-
rated and embellished by McEvily and Bond (184) and Pugh and associates
(185, 186, 187) for copper base alloys. Essentially, this model in-
volves the initial formation of a thick film; this film is then rup-
tured by a brittle process. The crack then propagates by a sequence of
"film formation followed by brittle rupture" process. This process has
been shown to not be operating on copper base alloys and since protec-
tive films on stainless steels are thin it does not apply to that system.

Another alternative to the simple slip dissolution process is the
"tunneling process: which was described initially by Nielson (188) for
stainless steels. Due to the work of Swann and coworkers (178, 189,
190, 191), Scamans and Swann (192) Dean and Staehle (193) Nielson (194),
and Scully and Harston (195) there is no doubt that the tunneling pro-
cess occurs, and that its occurrence corresponds with the incidence of
SCC in some alloys including stainless steel.
There is a great deal of evidence which suggests that the formation and subsequent rupturing of films on metals and alloys is a necessary requirement for an alloy to undergo SCC. For this reason it is felt that the slip dissolution model of SCC is the most viable and also the most useful model for understanding the SCC phenomenon which is available at this time.

During the slip process, dislocations either remain in a single slip plane (coplanar) or they may cross slip on intersecting slip planes. Two essential themes have been proposed for explaining how dislocation coplanarity can be used to rationalize the effect of alloy composition on susceptibility to SCC. The first, by Robertson and Tetelman (196) proposed that a high stacking fault energy enhances susceptibility to intergranular cracking because it would be possible in such instances to preferentially develop a high normal stress at the grain boundaries. A sufficiently high normal stress together with susceptibility of the alloy to undergo intergranular attack would be the criterion for intergranular cracking. Transgranular cracking could occur at structurally reactive static sites which are associated with dislocation pileups at Cottrell-Lomer barriers.

The second theme, proposed by Swann and coworkers (197, 198), presents arguments which favor dislocation coplanarity as an important factor in determining the susceptibility of a given alloy to cracking. These arguments suggest that transgranular cracking is associated with slip step emergence. A high degree of coplanarity gives a more discrete step having a greater probability of breaking the surface film; whereas the lower degree of coplanarity would produce a much less discrete break in
the surface with the result that the surface film may not be broken sign-
nificantly, Swann (21) presents evidence that austenitic stainless
steels which are susceptible to cracking, due either to impurities or
to nickel concentrations, exhibit strong tendencies toward coplanar dis-
location arrays.

One of the mechanisms which is often proposed as a cause of SCC in
austenitic stainless steels is the hydrogen embrittlement of the steel.
The main ideas embodied in the hydrogen embrittlement mechanism are (4):

(1) The primary cathodic reaction during the SCC process is hy-
drogen ion discharge at the tip of a crack.

(2) The hydrogen is absorbed locally, embrittling the crack tip
which then allows cracking to proceed more easily.

(3) The generally accepted embrittling mechanism is the formation
of a "quasi-martensite" or a hydride phase.

Most of the objections to the hydrogen embrittlement mechanism have
been presented in detail by Staehle (3) and Theus and Staehle (4). The
statements given below summarize these arguments.

(1) Transgranular SCC has been observed in alloys where martensit-
ic transformation is highly unlikely.

(2) Additions of hydrogen poisons to test media for the purpose
of enhancing hydrogen embrittlement through cathodic charging have in-
crease failure times of susceptible alloys rather than decreasing them.

(3) A correlation between hydrogen permeation rate and SCC as a
function of potential reportedly does not exist for 304 stainless steel.

(4) Embrittlement of a material does not necessarily lead to an
increased susceptibility to SCC.
(5) Tests on bonded composite materials have shown that susceptibility to SCC is not a function of hydrogen diffusivity or solubility.

(6) Uhlig et al (199, 200) have shown that the hydrogen embrittlement behavior in a metal is altered by the rolling direction of a cold worked susceptible alloy; whereas the SCC behavior of a cold worked alloy is independent of the rolling direction.

Additional evidence which vitiates the hydrogen agreement is that the susceptibility to SCC of many alloys increases with increasing temperature and probably the most compelling argument is the dependence of SCC upon the applied potential in both initiation and propagation modes.

For the particular case of cracking of 304 stainless steel in high purity-high temperature water it is doubtful that hydrogen embrittlement is the dominant mechanism of attack. Although there may be some hydrogen present under deaerated conditions, at the temperatures of concern I think any embrittling effect would be minimal.

The SCC of annealed plus sensitized stainless steels in high temperature, high purity water consists of an initiation phase and a propagation phase. Utilizing scanning electron microscopy on pre-polished Type 304 samples, Clarke, Danko, and Gordon (201) were able to determine that second phase particles located at grain boundaries were a key feature in the nucleation of IGSCC. The polished samples were exposed to $288^\circ C$ oxygenated water $3.1 \times 10^{-3} M O_2 (100 \text{ ppm } O_2)$ for various lengths of time in both the stressed and unstressed conditions. It was observed that the second phase grain boundary precipitates would dissolve preferentially at the particle-metal boundary. On stressed samples the same effect was seen; with the additional observation at short time,
that intergranular cracks were emanating from the crevice generated between the particle and the metal matrix. The grain boundary precipitates were identified as both titanium carbides and silicon rich particles (201).

At oxidizing potentials in acid solution, titanium carbide is not stable and dissolves at a high rate (49). In high temperature, oxygenated water, titanium carbide probably behaves similarly. Although all particles show evidence of dissolution, only those particles that are located at the grain boundaries initiate stress corrosion cracks in sensitized stressed samples.

The importance of the dissolution of second phase grain boundary precipitates is twofold (49). First, the crevice generated between the particle and the grain boundary probably generates an acid condition in the less corrosion-resistant, chromium depleted area. Secondly, the stress (strain) state at the bottom of the crevice is more severe than that of the bulk of the sample. Thus, a severe chemistry and stress state are localized to produce propagation in only selected areas.

In restricted crevice geometries, an acid condition should occur in Fe-Ni-Cr alloys even though the bulk solution pH remains neutral (or even basic) (202). The acidity arises because of the hydrolysis of metal corrosion products (203). In addition to the acidity, electrochemical neutrality of the solution requires that anions should concentrate in the crevice to compensate for the $\text{H}^+$ hydrolysis product.

Cowan (204) attempted to measure the pH in artificial stainless steel crevices in $288^\circ $C oxygenated water by bleeding out the crevice solution through a small capillary and measuring the pH with indicator
papers. The values obtained were in the range of 4 to 4.5 and could be considered an upper limit for the actual crevice pH because of probable dilution effects during sampling. DePaul (85) has shown unstressed, high-carbon, severely sensitized, stainless steel will suffer intergranular corrosion in acid solution (pH=3 to 4) in oxygenated water at 315°C. No attack was found in neutral or basic solutions.

The dominating factor in the IGSCC of sensitized austenitic stainless steel in high purity water is the inherent reactivity associated with the chromium depleted zone adjacent to the grain boundaries. The importance of this was discussed in Section 2.1.4 and it will be discussed further in Section 4.0. The low chromium content of the depleted region allows dissolution to occur which in the presence of a tensile stress results in IGSCC.
3.0 MATERIALS, EQUIPMENT, AND PROCEDURES

This section discusses the materials, equipment and procedures employed during the investigation.

(1) Materials: The composition and heat treatment procedures are discussed and also a description of the tests used to characterize the materials' susceptibility to intergranular attack is given.

(2) Equipment: Descriptions of the various pieces of equipment that were used in the course of the investigation are presented in this section.

(3) Procedure: The procedure section is divided into two parts. The first part describes the general procedures and techniques used throughout the testing program. The second part of this section describes the procedures that were used sporadically for specific purposes, i.e. Auger analysis metallography.

3.1 Materials

3.1.1 Chemistry and Specimen Geometry

The material used in this investigation was Type 304 stainless steel which was supplied by the Viking Steel Company of Cleveland, Ohio. Ninety pounds of the 6.35mm round by 3.66m ft. rod stock was purchased from Viking Steel and delivered in the annealed and cold drawn condition. The material was purchased according to ASTM-A479.

The certified chemical and physical analysis of the material as shipped by Viking Steel is given below:
The dimensions of the specimen chosen for use in this investigation are given in Figure 45. The specimens were prepared by the Weiss Precision Laboratory of Sunbury, Ohio and the Jordan Machine Shop of Grove City, Ohio.

During the course of the investigation, three different methods of heat treating were used. The temperatures and times used for the heat treatments have been the same for all methods. The material was annealed at 1050°C for 30 minutes and then water quenched. The material to be sensitized was then reheated to 650°C and held at that temperature for 1 hour at which time it was then removed from the furnace and allowed to air cool. Prior to all heat treatments the specimens were thoroughly degreased with acetone.

The first method of heat treating the specimens required encapsulation of the specimens in a quartz tube backfilled with argon and then proceeding with the heat treatments in a Lindberg Hevi Duty tube.
Figure 45

Dimensions of test specimen

- 13" (330.2 mm)
- 0.75" 0.25-28 Threads (19.1 mm)
- 0.25" (.64 mm)
- 0.25" Radius (0.64 mm)
- 0.1" Diameter (2.54 mm)
- 0.5" (12.7 mm)
- 2.375" (69.9 mm)
furnace. The method was discontinued due to a concern about the quench rate. The argon in the tube was preventing heat transfer and that the specimen was spending too long a time in the sensitization range. Most of the specimens heat treated in this manner were used in the early stages of the investigation where "bugs" in the rest of the test setup were being eliminated and they therefore did not influence the main body of data generated by this investigation.

The second heat treating procedure used was performed by the Electric Heat Treating Company of Columbus, Ohio. They heat treated the specimens in salt baths at the appropriate temperatures. Examination of the specimens after testing, utilizing a scanning electron microscope (SEM), revealed that surface damage caused by corrosive attack of the specimens in the salt bath had occurred prior to SCC testing. The samples had experienced attack to a depth of approximately .05mm. This was confirmed when a sample, fractured in air, exhibited the same crazing.

Approximately 20 samples had been heat treated in the salt baths so it was decided that in order to use the specimens the depth of the damage caused by the salt should be determined and then the remaining samples should be polished until all of the damaged material had been removed. Through alternate steps of mechanical polishing and Auger analysis it was determined that the damaged material could be removed if .102 mm were removed from the radius of the specimens. This was done to all of the remaining samples that had been heat treated in the salt baths. Most of the data generated with these "pre-cracked" samples is not included in the analysis of the main body of the data; however, in
a few instances its inclusion is beneficial. Whenever the data obtained with the samples heat treated in the salt baths is used, the data will be clearly marked.

The third heat treatment procedure, which was used on the samples providing the main body of the data, involved heat treating the samples in a Lindberg Hevi Duty Laboratory Furnace under an atmosphere of flowing argon. The samples were not encapsulated. Prior to insertion in the furnace the samples were degreased with acetone and then approximately 0.025 mm was removed from the diameter of the specimens by polishing with emery paper. This was done with hope of minimizing the effects of any residue remaining on the surface as the result of the cutting oils used in the machining of the specimens. During the Auger analysis of the samples heat treated in the salt baths, it was observed that rather large amounts of sulfur were present on the surfaces of the specimens. It was felt that some of this sulfur would be removed by polishing prior to heat treatment.

Following all three methods of heat treatment it was necessary to remove the oxide layer developed during actual heat treatments. The samples were first degreased with acetone to remove any residue adhering to the surface. The specimens were then polished with 600 grit silicon carbide emery paper. The amount of material removed from the diameter of the specimen was no more than 0.025 mm. After this final polish the specimens were again degreased with acetone and finally rinsed with double distilled water prior to loading in the autoclave for testing.
3.2 Equipment

The tests to determine the effect of temperature and oxygen on the stress corrosion cracking (SCC) susceptibility of Type 304 stainless steel in high-temperature high-purity water were conducted in a refreshed autoclave system. The schematic of the entire system is presented in Figure 46. The various components of the system are discussed in detail in this section.

3.2.1 Water Chemistry

High purity water was selected as the test solution. The environment was selected because there was a need to know the effects of a temperature and dissolved oxygen concentration of the SCC susceptibility of sensitized stainless steels in high purity water. The nuclear industry is particularly concerned with this alloy environment system. The water used in the investigation was of high purity, having a resistivity in excess of 1M ohm-cm. A breakdown of the water chemistry of an actual BWR is presented in Table 5. This quality of water was achieved and maintained in the laboratory through the use of three pieces of equipment described in the following sections.

3.2.1.1 Barnstead Still

Water exiting the Barnstead still is equivalent to single distilled water. The water has a resistivity of 578,000 ohm cm.

3.2.1.2 Millipore Super Q System

Water from the Barnstead still is passed through several ion-exchange and filtration cartridges manufactured by the Millipore Corporation. The Millipore Corporation describes their Millipore Super Q System as follows:
Figure 4B. Schematic Diagram of the Refreshed Autoclave Test Facility

1  Storage Tank  
2  Diaphragm Pump  
3  Millipore System  
4  Solenoid Valve  
5  Storage Tank  
6  Mixing Tank  
7  Storage Tank  
8  Micro-Pump  
9  Beckman Dissolved Oxygen Analyzer  
10  Gas Proportioner  
11  High Pressure Metering Pump  
12  Preheater  
13  Autoclave  
14  Pressure Gauge  
15  Cooler  
16  Back Pressure Regulator  
17  Collection Tank  
18  Drain
<table>
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<tr>
<th>Operating Mode</th>
<th>Boiling</th>
<th>Superheat</th>
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<td>Maximum Temperature of Fuel Element Wall, F</td>
<td>644-842</td>
<td>878-932</td>
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<tr>
<td>Maximum Coolant Flow Rate, lb/h</td>
<td>1540-2200</td>
<td>1320</td>
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<tr>
<td>Operating Pressure, psi</td>
<td>1420</td>
<td>1270</td>
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<td>t&lt;sub&gt;sat&lt;/sub&gt;</td>
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<tr>
<td>Quality at Exit %, at Channel Exit</td>
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<td>t&lt;sub&gt;sat&lt;/sub&gt; 698</td>
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<tr>
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<td>0.6-1.1</td>
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</tr>
<tr>
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<td>0.1-0.15</td>
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<td>0.3-0.5</td>
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<tr>
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"The Millipore Super Q is a modular system for producing water of extremely high purity, free from ionic contamination up to an 18 megohm-centimeter resistivity level, and free from particulate and microbiological contamination to an absolute size level determined by the pore size of the Millipore filter used.

A Super Q system consists basically of disposable cartridge elements in housings of modular design, joined together without connecting piping, and functioning in series. Individually, these elements provide organic adsorption, deionization, and final Millipore filtration to particle retention levels ranging from .22 to 1.2 micrometers. The full flow of effluent water passes through a temperature-compensated (25°C) Meg-O-Meter which monitors resistivity over an effective range from .5 to 18 megohm-centimeters."

The output flow rate of the unit is 1.5/hr. Our particular unit consists of four cartridges. The four cartridges function as described below:

(1) Super-C Cartridge: Organic contaminants are removed in this cartridge by adsorption in a cylindrical bed of granular activated carbon.

(2) Two Ion-Exchange Cartridges: Ionic contaminants are removed by this pair of cartridges. The contaminants are removed by ion exchange in a highly efficient mixed bed of strong acid and strong base resins that do not need regeneration.

(3) Millitube MF Cartridge: Placed as the final water treatment element in the Super Q System, this cartridge removes any microscopic particles or microorganisms that may have escaped retention by the
preceding upstream elements. The pore size of our membrane is .22 micrometers.

The water exiting the Millipore Super Q System has the following guaranteed analysis:

Dissolved Inorganics (ppm CaCO$_3$) less than .025

Specific Resistance (megohm-cm 25°C) 18

Silicate (ppm) less than .01

Heavy Metals (ppm) less than .01

Dissolved Organics (ppm) less than 1

Microorganisms/ml Particles larger than .22 removed by filter

Particles 5μm/ml Particles larger than .22 removed by filter

Spectrophotometric analysis of Water Produced by a Milli-Q System:

<table>
<thead>
<tr>
<th>Element</th>
<th>ng·g$^{-1}$</th>
<th>Element</th>
<th>ng·g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.1</td>
<td>Mg</td>
<td>0.5</td>
</tr>
<tr>
<td>Sb</td>
<td>0.5</td>
<td>Mn</td>
<td>0.05</td>
</tr>
<tr>
<td>Be</td>
<td>0.005</td>
<td>Hg</td>
<td>1</td>
</tr>
<tr>
<td>Bi</td>
<td>0.1</td>
<td>Mo</td>
<td>0.1</td>
</tr>
<tr>
<td>B</td>
<td>3</td>
<td>Ni</td>
<td>0.1</td>
</tr>
<tr>
<td>Cd</td>
<td>0.1</td>
<td>Nb</td>
<td>0.1</td>
</tr>
<tr>
<td>Ca</td>
<td>1</td>
<td>Si</td>
<td>0.1</td>
</tr>
<tr>
<td>Cr</td>
<td>0.1</td>
<td>Ag</td>
<td>0.01</td>
</tr>
<tr>
<td>Cu</td>
<td>0.2</td>
<td>Sn</td>
<td>0.1</td>
</tr>
<tr>
<td>Ga</td>
<td>0.2</td>
<td>Ti</td>
<td>0.1</td>
</tr>
<tr>
<td>Ge</td>
<td>0.5</td>
<td>V</td>
<td>0.1</td>
</tr>
<tr>
<td>Fe</td>
<td>0.2</td>
<td>Zn</td>
<td>0.1</td>
</tr>
<tr>
<td>Pb</td>
<td>1</td>
<td>Zr</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The output of the Millipore Super Q system is divided as it exits. Part of the effluent is pumped into a storage tank and the remainder is recirculated through the system so that further polishing of the water can take place.
3.2.1.3 **Storage and Transfer Tanks**

After exiting the Millipore system, the water is transferred to a 190 liter 316 Stainless Steel holding tank manufactured by Davis Heliarc. This tank is continuously sparged with argon. This storage tank feeds two refreshed autoclave systems, each system containing two 3.79 liter autoclaves. The high purity water is transferred from the storage tank to a 95 liter 316 stainless steel mixing tank (See Figure 47). Major changes in the dissolved oxygen concentration of the water are made in the mixing tank. The concentration of dissolved oxygen in the tank is controlled with the help of a Matheson Gas Proportioner. The gas proportioner pre-mixes the argon and oxygen in the desired proportions prior to their entry into the mixing tank. The gas mixture is bubbled into the mixing tank through a Teflon "fritte". By sparging with various mixtures of argon and oxygen gas the dissolved oxygen content of the water can be varied continuously from

When the high purity water has achieved the proper concentration of dissolved oxygen (measured with Beckman dissolved oxygen analyzer) the water is transferred into a final 114 liter 316 stainless steel storage tank. The dissolved oxygen concentration of the water is maintained at the desired concentration by continuously sparging this tank with the same mixture of argon and oxygen as was used in the mixing tank. The oxygen control system and transfer system is shown in Figure 48. The automatic oxygen control and water transfer system functions as follows:

1. When the water level in the mixing tank is low, the level control activates a solenoid valve which allows water to flow from the 190 liter storage tank into the 95 liter mixing tank. Water entering the
Figure 47 Schematic Diagram-95 liter Mixing Tank
Schematic diagram - oxygen control and transfer system
mixing tank is subjected to continuous sparging by the appropriate argon-oxygen gas mixture,

(2) Transfer of the high purity water from the mixing tank to the final storage tank is dependent upon two restraints:

(a) The oxygen concentration of the water must be above a pre-set value. This operation of the control device was altered on occasion depending upon whether the dissolved oxygen concentration of the water entering the mixing tank was to be raised or lowered.

(b) The water level of the final storage tank must be below a pre-set level.

When the two conditions described above are met simultaneously then the high purity water is transferred to the final storage tank from the mixing tank.

Three auxiliary control features were also designed into the control system. The first is that oxygen monitoring can be easily switched from the storage tank to the mixing tank and vice versa. There is also an override switch which can prevent transfer of water from the mixing tank to the 114 liter storage tank. Another switch controls a solenoid valve which allows manual filling of the mixing tank from the 190 liter storage tank.

3.2.2 Measurement of Dissolved Oxygen Concentration

Four separate techniques, as described in the following four sections, were used to determine the dissolved oxygen concentration of the water (199).

3.2.2.1 Beckman Model 735X Dissolved Oxygen Analyzer

The Beckman oxygen analysis system is a closed loop system consisting of an analyzer, a micro-pump to provide the necessary flow rate of
4.2 cc/sec, and an amplifier and direct readout console (Figure 49).

The heart of the system is the sensor which consists of a gold cathode, a silver anode, a Teflon membrane, and 4N KCL as the electrolyte. As the solution impinges on the membrane, some of the dissolved oxygen diffuses through the Teflon. This oxygen reacts with the KCL to produce KOH and a small current which is proportional to the dissolved oxygen in the water. The current is amplified and then calibrated to give a signal which is proportional to the dissolved oxygen.

The concentration of dissolved oxygen in the water was constantly monitored, both inlet and outlet, with the Beckman analyzer. When the analyzer is well calibrated the results obtained with the Beckman analyzer are reliable. However, the Beckman analysis was always verified with at least one chemical technique in order to provide increased certainty of the dissolved oxygen concentration of the water. The Beckman analyzer is designed to operate in the ppb oxygen range; however, with the aid of the calibration chart of Figure 50 the range of the instrument can be extended to about 3.1x10^{-6} M O_2 (10 ppm O_2).

3.2.2.2 Indigo Carmine Technique

The Indigo Carmine Technique is applicable to water containing less than 1.8x10^{-6} M (60 ppb) of dissolved oxygen, such as steam condensate and deaerated boiler feedwater. Dissolved oxygen reacts with the indigo carmine solution to produce a progressive color change from yellow-green through red to blue and blue-green. The result of each test can be determined by comparison of color developed in the sample with color standards made up to represent different concentrations of dissolved oxygen. There is little problem with interferences with this technique.
Figure 49
Schematic diagram - Beckman dissolved oxygen analysis system
Calibration Chart for Beckman Analyzer

Figur: 50  Calibrated chart for Beckman analyzer
when used in high purity water.

3.2.2.3 Winkler and Modified Winkler Technique

Depending upon the method employed for sampling, the technique is applicable to industrial water containing more than $1.6 \times 10^{-7}$ M or $1.6 \times 10^{-5}$ M (5 ppb or 500 ppb) of oxygen and having low concentrations of reducing and oxidizing materials. The sampling must take place in a specially prepared container if one wishes to make determinations of the dissolved oxygen concentration when small amounts of oxygen are present. After the sample has been collected, the free iodine liberated in an amount equivalent to the oxygen in the sample is titrated with thiosulfate using starch as an indicator.

3.2.2.4 Chemets

Chemets are disposable glass ampoules manufactured by Chemetrics, Inc., which are used for instant colorimetric analysis of water. Each Chemet contains a carefully measured quantity of a color forming reagent and it is sealed under a vacuum. Breaking the tip of an ampoule under the surface of the water causes the water to enter the tube and mix with the reagent. Color comparisons are then made.

For measurements of dissolved oxygen concentration in the 0 to 3.8 \times 10^{-4} M (0 to 12 ppm) range an acidic Indigo Carmine solution is used which reduces the amount of interference from copper, calcium, and magnesium. It also eliminates virtually all of the commonly encountered interferences which plague the Winkler titration test. The test method requires no correction for temperature, pressure, salinity, or dissolved gases as necessary when using a galvanic cell (membrane type) dissolved oxygen meter.
For determination of dissolved oxygen in the low ranges of 0 to $3.1 \times 10^{-5} \text{M}$ (0-1 ppm), $0 - 3.1 \times 10^{-6} \text{M}$ (0-100 ppb), and $0 - 1.3 \times 10^{-6} \text{M}$ (0-40 ppb) a new colorimetric reagent called Rhodazine D is used, which is pale yellow in reduced form, but reacts with oxygen to produce a reddish-violet solution. Color development is instantaneous. Snapping the tip of the sealed Chemet in the flowing sample stream provides a simple and reliable means of avoiding unwanted oxygen contaminants during the analysis.

3.2.3 High Pressure Refreshed Autoclave System

The various components comprising the high pressure portion of the refreshed autoclave test facility are numbered 1 through 18 in Figure 46. The separate components are described below.

3.2.3.1 Yarway High Pressure Positive Displacement Diaphragm Pump

The high purity water contained in the 95 liter storage tank enters the Yarway High Pressure Pump and it is then pumped through the high pressure autoclave system. Teflon is used as a diaphragm in the Yarway High Pressure Pump. Other than the Teflon diaphragm, all other parts of the pump which the high purity water comes in contact with are made of 316 stainless steel. The pump has a rated capacity of $22 \text{MN/mm}^2$ (3200 psi). At out operating conditions of $7.6 \text{MN/mm}^2$ (1100 psi) the flow rate is 3.8-5.7 lph.

3.2.3.2 Preheater

The high purity water flows under pressure from the high pressure pump into the pre-heater (See Figure 51). The preheater consists of an inner coil of approximately 18.3 m of 3.2 mm O.D. 316 stainless steel tubing which has been coiled around an asbestos covered pipe.
Figure 51 Preheater
Surrounding the coiled tubing are two Briskheat heating jackets. The lower heating jacket is controlled by a powerstat and the upper heating jacket is controlled by an on-off temperature controller. Each preheater is capable of 2500 watts and temperatures of 343-399°C.

3.2.3.3 Autoclaves

The vessels providing the containment for the actual test solution and test specimens are two 316 stainless steel autoclaves provided by the High Pressure Products Corporation (See Figure 52).

3.2.3.4 Cooler

Water exiting the two autoclaves must first be cooled before it can be passed through the back-pressure regulator. The cooler is a counter-current heat exchanger as shown in the schematic of Figure 53. The heat exchanger shell was fabricated by the Davis Heliarc Co., Columbus, Ohio. Approximately 13.7m of coiled 3.2mm O.D. 316 stainless steel tubing is contained within the cooler.

3.2.3.5 Back Pressure Regulator

The final component of the high pressure system is the back pressure regulator. This device allows for adjustment of the operating pressure of the system. Water exiting the back pressure regulator is unpressurized and proceeds to an accumulation tank. Two types of back pressure regulators were used during the course of the experimental program. Initially a back pressure regulator manufactured by the Consolidated Controls Corporation was used. This back pressure regulator was not well suited for our requirements however because it was designed for higher flow rates. Therefore a new back pressure regulator was purchased from the Tescom Corporation which was designed to operate at low flow
Figure 52
Type 316 stainless steel autoclave
Figure 53  Cooler
rates and inlet pressures of up to 17.2MN/mm^2. The new pressure regulator has worked quite well.

3.2.4 Constant Extension Rate Testing Machines

Two constant extension rate machines designed by W.J. Nutter and P.D. Carter were utilized in the testing program (See Figure 54). The constant extension rate machine is a model P-2000. The constant extension rate machine is composed of the following components:

(1) A constant speed motor provides the necessary power for the straining of the specimen.

(2) The power of the motor is transmitted to the specimen through a series of gear reducers. The first gear reducer is a variable reduction unit with ratios from 1:1 to 50:1. The second reduction unit has a fixed ratio of 900:1. The third reduction unit has a worm and pinion gear with a ratio of 60:1 which converts the rotary motion of the motor to vertical motion which provides a method of straining the specimen. The final means of reduction is a shaft with 18 threads per 25.4 mm which is driven by the worm and pinion gear.

(3) The combination of the various motor speeds and gear ratios makes it possible to achieve cross head velocities from 1.27x10^{-5} mm/sec to 1.27x10^{-3} mm/sec. Calculation of specimen strain rates are presented in Appendix C.

3.2.5 Recording and Measurement Devices

3.2.5.1 Measurement of Load

One of the variables of interest in the testing program is the load applied to the specimen. The load on the sample is determined with the use of a calibrated load cell. The load cell is activated with a
Figure 54

Constant extension rate testing machine - P-2000
specific voltage and puts out a corresponding voltage in proportion to the applied load on the sample. The output voltage from the load cell is fed into a signal conditioner where the signal is amplified. This amplified signal is fed into a recorder where the graph of load vs. time is produced. The dual pen recorders used in this study were manufactured by the Leeds and Northrup Corporation. Occasionally an Esterline Angus recorder was also used to monitor the load on the specimen. The signal conditioners were manufactured by the Sensotec Co. and the Daytronics Corp. The load cells were made by BLH Electronics.

3.2.5.2 Measurement of Specimen EMF

It was determined that the open circuit potentials of the specimens should be measured as a function of time. This was accomplished through the use of a Ag/AgCl reference electrode, a Keithly 602 electrometer and a recorder.

Figure 55 is a schematic drawing of the Ag/AgCl high temperature reference electrode which was designed so that it could be inserted directly into the autoclave. The Ag/AgCl reference electrode was chosen because of its compatibility with the test solutions, its stability up to 290°C, and the practical experience developed in its use by other researchers.

The Ag/AgCl reference electrode is constructed as follows:

1. The silver wire used is of high purity (99.99%) so as to minimize interfering reactions.

2. The wire is polished with emery paper and then rinsed with acetone and double distilled water.

3. The wire is then placed in a 1N hydrochloric acid solution.
Schematic drawing of the Ag/AgCl high temperature reference electrode
The silver wire is made the anode and a platinum gauze is made the cathode. Using a D.C. power supply, a current of about 15 mA is passed for a period of about 12 hours or more.

(4) After chloridizing, the Ag wire is inserted in to the 6.35mm Teflon tubing which forms the main compartment of the reference electrode. The high pressure fittings are assembled at this time.

(5) The chamber is filled and rinsed with .01N KCL several times.

(6) Zirconia sand is then packed into the main chamber of the reference electrode. This is done to remove air bubbles and also to provide a greater diffusion barrier to extraneous ions. A Teflon plug is then inserted into the main compartment.

(7) The potential of the electrode with respect to a saturated calomel electrode is checked at this time. The correct reading should be +100mV.

(8) The barrel of the Teflon buffer compartment is now screwed into place.

(9) The buffer compartment is rinsed several times with double distilled water and then filled with zirconia sand that has been washed with distilled water. This sand provides for an increased diffusion path for extraneous ions and also decreases the chances of contamination of the test solution from the reference electrode.

(10) A Teflon plug fitted with a 1.6mm zirconia tube is screwed onto the end of the buffer compartment.

(11) The completed reference electrode is again checked against a saturated calomel reference electrode. The correct reading is now +80 mV.
(12) The assembled reference electrode is now ready to be inserted into the autoclave.

The working electrode in this system is the test specimen. The test specimen is isolated from the autoclave through the use of Teflon fittings and inserts.

Final electrical isolation of the specimen is achieved by isolating the plate holding the straining mechanism from the rest of the test stand. This is accomplished through the use of Teflon washers and insulating paint.

After the reference electrode has been inserted into the autoclave, a Keithly Electrometer Model 602 is used to measure the potential difference between the working electrode (the specimen) and the Ag/AgCl reference electrode. The output of the electrometer is fed into a Leeds and Northrup recorder so that a record of the open circuit potential as a function of time is obtained.

3.2.5.3 Measurement of Solution Conductivity and pH

Spot checks of the conductivity of the test solution were made with a Beckman Model 16C conductivity bridge and probes with cell constants of .01, .1, and 1. The pH of the test solution was checked occasionally with a Beckman Model 3550 pH meter.

3.3 Procedure

This section is divided into two parts. The first part describes the general procedures that were used throughout the testing program. The second part of the section deals with the procedures that were only used to answer specific questions.
3.3.1 General Procedures

The main body of data contained in this thesis was obtained over a two year period. During that time several changes in the operating procedure were made. In order to provide an understandable basis for these changes, the procedures used in the program are presented in chronological order starting with the initial static autoclave testing.

3.3.1.1 Static Autoclave Testing

The general procedure for the start up and operation of a constant extension rate test (CERT) in a static autoclave is as follows:

1. The interior of the autoclave and the autoclave head assembly is degreased with acetone.

2. Double distilled demineralized water is added to the autoclave to the appropriate level.

3. The specimen to be tested is loaded in the autoclave head (See Figure 56). The specimen is electrically isolated where it exits the autoclave with a specially machined Teflon insert (See Figure 57) and it is electrically isolated from the stressing jig with a Teflon washer and shrinkable Teflon (See Figure 58).

4. The autoclave head is placed into position and the ten head bolts of the autoclave are torqued to approximately 170 Nm.

5. No monitoring of the open circuit potential of the specimen is undertaken during the static autoclave tests.

6. The automatic temperature controls are set to the desired settings.

7. The autoclave is allowed to reach the desired temperature.
Figure 56 Test specimen loaded in head of autoclave.
Figure 57

Electrical isolation of specimen where it exits the autoclave
Figure 58

Electrical isolation of specimen on the interior of the autoclave.
(8) The straining apparatus is started and the CERT test is begun.

(9) Following failure of the specimen, the straining apparatus is turned off, and the temperature controls are turned off.

(10) The autoclave is allowed to cool (Approximately 12 hours). The autoclave head is then removed and the failed specimen is removed from the autoclave and placed in a specimen box for storage.

The concentration of dissolved oxygen in the autoclave is calculated in the manner described in Appendix D.

3.3.1.2 Refreshed Autoclave Testing

The general procedure for the start up and operation of the refreshed autoclave test facility is described below:

(1) The desired mixture of argon and oxygen is bubbled through the mixing and storage tanks until the desired concentration of dissolved oxygen is achieved in both tanks. The concentration of dissolved oxygen is determined through use of one or more of the test methods described in Section 3.2.2.

(2) The test specimen's initial diameter and initial gauge length is measured. The specimen is then degreased with acetone. The sample is then mounted in the head of the autoclave (See Figure 56). The electrical isolation is shown in Figure 57, 58, and 59.

(3) The specimen is checked with a Simpson meter to be sure that it is electrically isolated from the autoclave head.

(4) Prior to putting the head of the autoclave in place, the inside of the autoclave and the specimen jig are cleaned and degreased with acetone. Just prior to putting the head of the autoclave in place, the specimen is again degreased with acetone and then rinsed with double
Figure 59 Electrical isolation of the test frame.
distilled water.

(5) The autoclave head is placed into position and the ten bolts tightened to approximately 170 Nm.

(6) The high pressure pump is started and the system is allowed to fill and operate unpressurized for approximately 1 hour.

(7) If the open circuit potential of the specimen is to be monitored as a function of time, then the reference electrodes are inserted into the autoclaves at this time.

(8) The system is then pressurized to 7.6 MN/mm².

(9) The automatic temperature controllers are set to the desired temperatures. The temperature controllers control the two preheaters and the 2 autoclave heating jackets.

(10) After the autoclaves have reached the desired temperatures, the CERT test is not begun until the open circuit potential of the specimen has stabilized. This generally takes from 12 to 24 hours.

(11) The desired strain rate is selected and the straining apparatus is started.

(12) After failure of the specimen, the high pressure pump is shut off and the pre-heater and autoclave heaters are also shut off.

(13) Following cool down of the autoclaves (approximately 12 hrs) the specimens are removed and placed in specimen boxes.

3.3.1.3 Routine Oxygen Analysis, Conductivity Measurement, and pH Determination

At least once during every test employing the refreshed autoclave system, the inlet and outlet oxygen levels were measured. The amount of dissolved oxygen in the inlet water stream was constantly monitored with
the Beckman Oxygen Analyzer. In the early stages of the testing program the Beckman analysis was supplemented with chemical analysis. Either the indigo Carmine test of the Winkler test was used depending upon the oxygen level being used at the time.

Spot checks were made of the conductivity of the water. Both the conductivity of the inlet and the outlet water of the autoclave was tested. No appreciable difference was ever found between the inlet and outlet water.

Spot checks were made of the pH of the water. Again, both the inlet and outlet water was checked and, as was the case with the conductivity measurement, there was never any appreciable difference between the two measurements. The pH measurement always indicated a neutral solution.

3.3.1.4 Scanning Electron Microscopy

The scanning electron microscope was the primary tool used in determining the type and extent of cracking that the samples had undergone when subjected to the various temperature and oxygen conditions. The fracture surfaces of the specimens were examined at low (30 to 50x) and high (7000x) magnifications.

3.3.2 Special Procedures

3.3.2.1 Metallography

Metallography has to be considered a special procedure for this study because only selected samples were examined. The samples selected were rough polished with 240, 320, 400, 600 grit carbide papers, mechanically polished on a Syntron unit with 1 micron diamond paste, and then finally polished with .05 micron alumina powder. The samples were
electrolytically etched with saturated oxalic acid.

3.3.2.2 Sensitization Tests

Four separate tests were conducted on two different heat treatment batches. The Huey test, Strauss test, and oxalic acid etch test were performed at the Ohio State University. Samples were sent to the Argonne National Laboratory for Electrochemical Polarization Reactivation (EPR) testing. All of the tests were conducted according to ASTM-A262-70.

3.3.2.3 Auger Analysis

Selected samples were examined with the Auger electra spectrometer at the Ohio State University.
4.0 EXPERIMENTAL RESULTS

4.1 Material Characterization

Type 304 stainless steel was used throughout the testing program. The material was used in both the annealed and in the annealed plus sensitized condition. The annealing procedure consisted of heating at 1050°C for 30 minutes and then quenching in water. Following the annealing procedure, if the material was to be sensitized, the material was reheated to 650°C for one hour and allowed to air cool. The choice of these particular heat treatment temperatures and times was based upon knowledge obtained by the General Electric Company and Toshiba of Japan (28, 97). Use of this sensitization treatment was expected to produce material which was at an intermediate stage of sensitization. The intermediate sensitization condition allowed accurate determinations of the effects of the test variables. A heavily sensitized sample would have masked the environmental effects on SCC and a lightly sensitized sample would not have been sufficiently susceptible to SCC to allow determination of the environmental effects on SCC.

In order to determine the degree of sensitization of the samples, the samples were subjected to four tests which reveal the susceptibility of austenitic stainless steels to intergranular corrosion due to carbide precipitation. The four tests employed were:
(1) Oxalic Acid Etch Test;
(2) Nitric Acid Test;
(3) Copper-Copper Sulfate-Sulfuric Acid Test;
(4) Electrochemical Polarization Reactivation Test (EPR).

All four tests were conducted on three different groups of test specimens. Material A was sensitized Type 304 stainless steel which had been heat treated at the Ohio State University. Material B was also sensitized Type 304 stainless steel but this material had been heat treated by the Battelle Columbus Laboratories. Material A and Material B were sensitized at 650°C for 1 hour following a 30 minute-;050^0C annealing treatment. Material C was also Type 304 stainless steel but this material was in the annealed condition.

4.1.1 Oxalic Acid Etch Test

The results of the oxalic acid etch tests are shown in Figures 60, 61, 62, and 63. Figure 60 shows the etch structure for material A which was heat treated at the Ohio State University. Figure 61 shows the etch structure of Material B which was heat treated at the Battelle Columbus Laboratory. Figure 62 depicts material C which was the annealed material. Material A and B clearly show a ditch structure in the near surface region indicating severe sensitization. At the center of the specimens the etch structures change for both materials A and B. Material A shows a dual structure while material B shows more of a step structure. This indicates that material A is more heavily sensitized than material B. This investigation also indicates that there is a sensitization gradient within the test specimens. The specimens are more heavily sensitized at the surfaces than at the interior. This is
Figure 60

Microstructure of Sample A after oxalic acid etch test
Figure 61 (Top)
Microstructure of Sample B after oxalic acid etch test

Figure 62 (Bottom)
Microstructure of Sample C after oxalic acid etch test
Figure 63
Comparison of etch structure of Sample A and Sample B after oxalic acid etch tests
shown clearly in Figure 63 for materials A and B.

The etch structure of the quench annealed material varies little from the surface to the center of the specimen (See Figure 62). The etch structure can be classified as a step structure with a few ditches.

Classification of etch structures is based on ASTM-A262 guidelines.

The reason for the different structures of material A and B is not known. The differences could have resulted from variations in the actual times at the sensitizing temperature which could have been brought about by different furnace geometries thereby resulting in different heating and cooling characteristics.

The difference in the degree of sensitization for material A and B is of minor importance due to the fact that material B was only used for initiation studies. The surface layers of material A and B appear to have undergone the same degree of sensitization and therefore they should be equally susceptible to crack initiation.

4.1.2 Nitric Acid Test

The nitric acid test is based on weight loss determinations and therefore provides a quantitative measure of the relative performance of the specimens evaluated. The nitric acid tests involve subjecting the test specimens to boiling nitric acid for five boiling periods of approximately 47 hours each with a fresh test solution being used in each period. The effect of the acid on the material was measured by determining the weight loss of the specimens after each test period and for the total of the periods. The results of the nitric acid test are shown in Table 6.
<table>
<thead>
<tr>
<th>Test Period</th>
<th>Sample Weight Loss (cm/month)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>1</td>
<td>65*</td>
</tr>
<tr>
<td>2</td>
<td>8.9</td>
</tr>
<tr>
<td>3</td>
<td>8.4</td>
</tr>
<tr>
<td>4</td>
<td>25.7</td>
</tr>
<tr>
<td>5</td>
<td>8.1</td>
</tr>
</tbody>
</table>

Total of all periods average* 12.7 14.2 6.7

*During the first test period excessive evaporation occurred. This caused the concentration of the nitric acid to increase which in turn increased the corrosive attack. The results of the first period are not included in the "all period average".
The results of the nitric acid test clearly show that samples A and B are more susceptible to intergranular attack than sample C. Sample B, which was heat treated at Battelle, appears to be slightly more susceptible to intergranular attack than sample A which was heat treated at the Ohio State University. The reason for this is not known.

In general, the samples are not heavily sensitized. They can be described as moderately sensitized. This is exactly the type of metallurgical structure that was desired at the beginning of the testing program.

4.1.3 Copper-Copper Sulfate-Sulfuric Acid Test

Samples A, B, and C were embedded in copper grindings exposed to boiling acidified copper sulfate solution for 24 hours and then bent 120°. Intergranular cracking or crazing on the surface of the bent specimen is evidence of susceptibility to intergranular corrosion. Samples A and B failed this test, indicating their susceptibility to intergranular corrosion.

4.1.4 Electrochemical Polarization Reactivation Testing

The EPR test used by General Electric to quantify the degree of sensitization of a particular material is described in Section 2.2.4. Samples of material A, B, and C were submitted to Argonne National Laboratory for EPR testing. The results are listed below:

<table>
<thead>
<tr>
<th>Specimen</th>
<th>EPR Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material A (Sensitized 304, OSU)</td>
<td>1.5</td>
</tr>
<tr>
<td>Material B (Sensitized 304, Battelle)</td>
<td>1.3</td>
</tr>
<tr>
<td>Material C (Quench annealed 304, OSU)</td>
<td>0.05</td>
</tr>
</tbody>
</table>
The significance of these EPR numbers is discussed in Section 5.0.

4.2 Control Tests—Conducted in Air

Prior to conducting tests in the chosen environment (high purity water), it was necessary to develop the baseline data of CERT tests conducted in an inert environment. The inert environment chosen for this study was air. This baseline data is necessary because results of CERT tests are generally expressed as ratios of mechanical properties measured in the environment to those in an inert environment.

The initial results of these air control tests are shown in Figure 64. It is obvious there is a great deal of scatter in this data. The reason for this is that initially a batch of samples was heat treated in salt baths. It was not discovered until after the testing that these samples had undergone intergranular attack in the salt baths. These intergranular cracks effectively lowered the cross sectional area of the specimens. If this reduced cross sectional area is taken into consideration by mathematically reducing the initial diameters of these particular specimens and using the "corrected" values in all subsequent calculations of stress, etc., the curves of Figures 65, 66, 67, and 68 result. Figures 65–68 show $\sigma_{UTS}$, $\%E$, $e_{UTS}$, and $e_\%$ as a function of temperature. It is obvious that the correction reduces the scatter in the data significantly. However, there is still too much scatter in the data to assign a unique value of $\sigma_{UTS}$, $\%$ elongation, etc., for each material and test condition at each temperature. Therefore, for each particular property at a given temperature, only one value has been selected for use in subsequent calculations. For instance, the ultimate tensile strength of sensitized as well as quench annealed material, when
Figure 64

Air control tests, not corrected
Air Control Tests
304 Stainless Steel
Corrected Values

Figure 55
Air control test, corrected values, $\sigma_{UTS}$ versus temperature.
Air Control Tests
304 Stainless Steel
Corrected Values

Figure 66
Air control test, corrected values, % elongation versus temperature
Air Control Tests
304 Stainless Steel
Corrected Values

\[ \epsilon_{UTS} \% \]

Temperature, °C

\[ \Delta \] Sen 304, \( \dot{\varepsilon} = 10^{-5} \text{ Sec.} \)
\[ \bullet \] Sen 304, \( \dot{\varepsilon} = 10^{-6} \text{ Sec.} \)
\[ \Downarrow \] QA 304, \( \dot{\varepsilon} = 10^{-5} \text{ Sec.} \)
\[ \blacksquare \] QA 304, \( \dot{\varepsilon} = 10^{-6} \text{ Sec.} \)

Fig. 2.17
Air control test, corrected values, \( \epsilon_{UTS} (%) \) versus temperature
Air Control Tests
304 Stainless Steel
Corrected Values

\[ \text{Figure 63} \]

Air control test, corrected values, \( e_f \) (%) versus temperature
tested at strain rates of either $10^{-5}$/sec or $10^{-6}$/sec, is approximately 70,000 psi. Based on the available data this is a reasonable assumption.

Figures 69-74 are SEM photographs of the fracture surfaces of samples tested in air. In Figures 72 and 73 the evidence of the intergranular attack which occurred during the salt bath heat treatment is clearly visible.

4.3 Crack Initiation Study

In order to establish the credibility of the values to be reported for $da/dt$ it was necessary to conduct a crack initiation study. There were three main areas of interest:

(1) Crack initiation where intergranular cracking had been observed in sensitized material;

(2) Crack initiation where transgranular cracking had been observed in sensitized material;

(3) Crack initiation in quench annealed material at high concentrations of dissolved oxygen (greater than $2.5\times10^{-5}$ M O$_2$) (800 ppb O$_2$).

The results of the study are shown in Figures 75 and 76. For sensitized material tested at $250^\circ$C with $2.5\times10^{-4}$ M O$_2$ (8 ppm O$_2$) the intergranular cracks initiated after about 6% strain. For sensitized material tested at $250^\circ$C with $1.55\times10^{-6}$ M (50 ppb O$_2$) the transgranular cracks initiated after 9% strain. Transgranular cracks initiated in quench annealed material tested at $250^\circ$C with $1.25\times10^{-4}$ M O$_2$ (4 ppm O$_2$) after about 25% strain.

For the purpose of calculating the crack propagation rates of the stress corrosion cracks, it was assumed that all intergranular stress
Figure 69 Quench annealed Type 304 stainless steel; 250°C, air
Figure 71 Sensitized Type 304 stainless steel; 250°C, air
Figure 71 Sensitized Type 304 stainless steel; 250°C, air
Figure 72 Sensitized Type 304 stainless steel; 175°C, air
Figure 73 Quench annealed Type 304 stainless steel, 150°C, air
Figure 74 Sensitized Type 304 stainless steel; 100°C, air
Crack Initiation Study-Crack Depth vs Time
304 Stainless Steel
\( \dot{\varepsilon} = 10^{-6}/\text{Second}, 250\degree\text{C} \)

Figure 75
Crack initiation study - Crack depth versus time
Figure 76

Crack initiation study, TCSCC, 250°C, $1.55 \times 10^{-6}$ M $\text{O}_2$ (50 pph)
corrosion cracks initiated after 6% strain, that all transgranular stress corrosion cracks in sensitized material initiated after 9% strain, and that all transgranular stress corrosion cracks in quench annealed material initiated after 25% strain. The actual strain necessary to initiate a stress corrosion crack is a function of the test temperature, strain rate and the dissolved oxygen concentration of the water.

4.4 Crack Propagation Rates

The measured crack propagation rate was chosen as the primary method of determining the susceptibility of the material to the test environment. The process used to determine the crack propagation rates is described in Section 3.3. This section includes the results of the crack initiation study, and the effect of dissolved oxygen concentration, temperature, specimen strain rate, and temperature and dissolved oxygen concentration on SCC susceptibility.

4.4.1 Sensitized Type 304 Stainless Steel

4.4.1.1 Effect of Dissolved Oxygen Concentration on SCC Susceptibility

The primary purpose of this investigation was to determine the effects of temperature and dissolved oxygen concentration on the susceptibility to cracking of Type 304 stainless steel in high temperature, high purity water. The effect of the dissolved oxygen concentration of the water on SCC behavior is presented in this section.

Oxygen concentrations used in the testing program ranged from $1.55 \times 10^{-7}\text{M } \text{O}_2$ (5 ppb) to $1x10^{-3}\text{M } \text{O}_2$ (32 ppm) at temperatures ranging from $150^\circ\text{C}$ to $290^\circ\text{C}$. Figures 77–80 illustrate the dependence of the crack propagation rate on the dissolved oxygen concentration at $290, 250, 200$, and $150^\circ\text{C}$. 
Estimated Crack Growth Rate vs Dissolved Oxygen Content

304 Stainless Steel, 290°C, $\dot{\varepsilon} = 10^{-6}$/Second

Figure 7

Estimated crack growth rate vs dissolved oxygen content, 290°C
Estimated Crack Growth Rate vs Dissolved Oxygen Content

304 Stainless Steel, 225° & 250°C, $\dot{\varepsilon} = 10^6$/Second

Figure 78

Estimated crack growth rate vs dissolved oxygen content, 250°C
Estimated Crack Growth Rate vs Dissolved Oxygen Content

304 Stainless Steel, 200°C, $\dot{\varepsilon} = 10^{-6}$/Second

- QA 304, Transgranular Cracking
- Sen 304, Intergranular Cracking
- Sen 304, Dual Mode Cracking
- Sen 304, Transgranular Cracking

Figure 79
Estimated crack growth rate vs dissolved oxygen content, 200°C
Estimated Crack Growth Rate vs Dissolved Oxygen Content
304 Stainless Steel, 150° & 175°C, ϵ = 10^-6 / Second

Figure 80
Estimated crack growth rate vs dissolved oxygen content, 150° and 175°C
Figure 81 is a composite plot including all of the test results. The figure is divided into two main zones. The two zones are labeled intergranular crack initiation and transgranular crack initiation and they are separated on Figure 81 by a band which is un-labeled. This corresponds to a region of uncertainty due to the uncertainty involved with the determination of the dissolved oxygen concentration of the water.

An additional zone labeled on Figure 81 is the zone entitled "dual mode cracking". Cracking which occurs within this region initiates intergranularly and eventually switches to a transgranular mode of cracking.

In figures 82-88 the effects of the dissolved oxygen concentration on the susceptibility to SCC at $290^\circ$C is presented. In Figures 82, 83, and 84 the dissolved oxygen concentration of the water was $1 \times 10^{-3} \text{M}(32 \text{ ppm})$. The fracture surface is 100% intergranular. SEM photographs for both of the fracture surfaces were taken of this specimen. There is a reasonably good match up of the photographs of the two surfaces. The fact that the match up is not perfect is evidence that dissolution of the metal took place during the test.

When the dissolved oxygen content is lowered to an inlet value of $4.6 \times 10^{-6} \text{M} (150 \text{ ppb})$ a dual mode of cracking was observed. Figures 85 and 86 show the details of this type of attack. The crack has clearly initiated in an intergranular fashion and then changed modes to a transgranular mode. The concentric rings on the transgranular fracture surface may be indicative of crack arrest and would therefore suggest a discontinuous crack advance process.
Composite Plot - Estimated Crack Growth Rate vs Dissolved Oxygen Content

304 Stainless Steel, $\dot{c} = 10^{-6}$/Second

Transgranular Crack Initiation
Intergranular Crack Initiation
250°C, Sen 304
200°C, Sen 304
290°C, Sen 304
250°C, QA 304

Figure 81
Composite plot - Estimated crack growth rate vs dissolved oxygen content, $\dot{c} = 10^{-6}$/sec
Figure 82
SEM photographs of fracture surface; Left half IGSCC
Figure 83
SEM photographs of fracture surface; Right half IGSCC
Figure 84
SEM photographs of opposing fracture surfaces
Figure 85

Sensitized Type 304 stainless steel, 290°C, 4.5×10⁻⁶ N₂O₂⁻ (150 ppm N₂O) (Inlet), Dual mode SCC
Figure 86

Sensitized Type 304 stainless steel, 290°C, $4.5 \times 10^{-6} \text{M} \text{O}_2$ (150 ppb $\text{O}_2$) (inlet), Dual Mode SCC.
Sensitized Type 304 stainless steel, 290°C, approx.
$1.2 \times 10^{-5} \text{ N}_2(400 \text{ ppb}) \text{ O}_2$.
Figure 88

Sensitized Type 304 stainless steel, 290°C, 7.5x10^{-7} M O_2 (25 ppm), IGSCC
Figures 87 and 88 are indicative of the type of behavior observed at oxygen concentrations below approximately $3.1 \times 10^{-6}$ M (100 ppb). The cracking is completely transgranular. As before, there are no indications of crack arrest on the transgranular fracture surfaces.

At the temperature of 250°C the same type of behavior is observed, i.e. a change from intergranular cracking to transgranular cracking as the dissolved oxygen concentration is reduced. As was the case for 290°C, the change in cracking mode again occurs at approximately $3.1 \times 10^{-6}$ M O$_2$ (100 ppb). The difficulty in determining the exact concentration of dissolved oxygen in the autoclave makes it impossible to assign a precise value to the oxygen concentration at which the change in cracking mode occurs.

Figures 89-93 illustrate the intergranular cracking which occurs in sensitized Type 304 stainless steel at 250°C with oxygen concentrations over $2.5 \times 10^{-5}$ M (800 ppb). Figures 90, 91, and 92 were used in the crack initiation study. Note that the cracks in their early stages are clearly intergranular. The sample shown in Figure 93 was tested at an oxygen concentration of $2.5 \times 10^{-5}$ M (800 ppb). Although primarily intergranular cracking was found there is some evidence of transgranular cracking in the interior of the specimen. Changes in the crack tip chemistry, stress intensity, or strain rate at the tip of the crack during crack propagation may be causing the change in fracture mode.

Figures 94 and 95 are SEM photographs of a sample tested at a dissolved oxygen concentration of approximately $6.25-7.75 \times 10^{-6}$ M (200-250 ppb) In, shows much more transgranular cracking than the specimen tested at $2.5 \times 10^{-5}$ M O$_2$ (800 ppb O$_2$) at the same temperature of 250°C.
Figure 89

Sensitized Type 304 stainless steel, 250°C, $2.6 \times 10^{-4} \text{M O}_2$ (8.5 ppm), IGSCC.
Sensitized Type 304 stainless steel, 250°C, $2.5 \times 10^{-4} \text{ M O}_2$ (8 ppm), Interrupted test.

Figures 90, 91, 92

Sensitized Type 304 stainless steel, 200°C, $2.5 \times 10^{-4} \text{ M O}_2$ (8 ppm), IGSCC.
Figure 93

Sensitized Type 304 stainless steel, 250°C, 2.6x10^{-5} M O_2
(800 ppb) O_2, Dual mode SCC
Figure 94

Sensitized Type 304 stainless steel, 250°C, 6.4x10^-6 M O_2
(225 ppb) (Inlet), Dual mode SCC
Figure 95

Sensitized Type 304 stainless steel, 250°C, 3.1x10^{-6} M O_2 (100 ppb) (Inlet), Dual mode See.
(Figure 93). Apparently, the conditions necessary to initiate the change in fracture mode from intergranular to transgranular are developed more rapidly as the dissolved oxygen concentration is lowered.

Figures 96-104 are SEM photographs which illustrate the transgranular cracking which is observed in Type 304 stainless steel when it is tested in high purity water at 250°C with less than approximately 3.1x10^{-6} M O_2 (100 ppb) dissolved oxygen. Figures 96, 97, and 98 are SEM photographs of both fracture surfaces of the same specimen. At low magnification as well as high magnification, there is an excellent match up of the photographs. This match-up indicates that dissolution of the material is occurring on a fine scale.

Figures 103 and 104 show transgranular cracks in the early stages of initiation. It should be noted again that in all cases of transgranular cracking there are marks on the fracture surfaces which are perpendicular to the direction of crack propagation.

Figures 105 and 106 are SEM photographs of specimens that were tested at 225°C in high purity water with 2.5x10^{-5} M O_2 (800 ppb O_2). Note again the presence of transgranular cracking at the tips of the cracks.

The two modes of cracking, intergranular and transgranular, also occur at 200°C. This is illustrated in Figures 107-111. Figure 107 shows the intergranular cracking that occurred at 2.5x10^{-6} M O_2 (8 ppm O_2). Figures 108-111 illustrate the transgranular cracking which occurs at oxygen concs: below approximately 6.25x10^{-6} M O_2 (200 ppb O_2). Photomicrographs of the transgranular cracks are shown in Figure 108. Note the blunt nature of the cracks.
Sensitized Type 304 stainless steel, 250°C, 4.5x10^{-5} M O_2
(150 ppb)(Outlet), TCSCC, Right half specimen
Figure 98

Sensitized Type 304 stainless steel, 250°C, $4.5 \times 10^{-6}$ M O$_2$ (150 ppb) (Outlet), TGSCC, Opposing fracture surfaces.
Figure 99 (Left)
Figure 100 (Right)

Sensitized Type 304 stainless steel, 250°C, \(4.5 \times 10^{-6} \text{ M O}_2\) (150 ppb) (Inlet), TGSCC.

Sensitized Type 304 stainless steel, 250°C, \(2.3 \times 10^{-6} \text{ M O}_2\) (80 ppb) (Inlet), TGSCC.
Sensitized Type 304 stainless steel, 250°C, $1.55 \times 10^{-6} \text{M O}_2$ (50 ppb), TGSCC
Sensitized Type 304 stainless steel, 250°C, 6.2x10^{-7} M O_2 (20 ppb), TGSCC.
Sensitized Type 304 stainless steel, 250°C, 7.5x10^{-6} M O_2
(250 ppb) O_2 (inlet)

Figures 103, 104

Sensitized Type 304 stainless steel, 250°C, 1.55x10^{-6} M O_2
(50 ppb), interrupted test
Figure 105 (Left)

Sensitized Type 304 stainless steel, 225°C, 2.5x10^{-5} M O_2
(300 ppb) O_2, Dual mode SCC

Figure 106 (Right)

Sensitized Type 304 stainless steel, 225°C, 2.5x10^{-5} M O_2
(300 ppb) O_2, Dual mode SCC
Sensitized Type 304 stainless steel, 200°C, 2.5x10^{-4} M O_2 (8 ppm O_2), IGSCC.
Figure 108

Sensitized Type 304 stainless steel, 200°C, 1.1x10^{-6} M O_2
(35 ppb)(Inlet), TOSCC.
Sensitized Type 304 stainless steel, 200°C, $7.5 \times 10^{-7}$ M O$_2$
(25 ppb), TGSCC.

Sensitized Type 304 stainless steel, $7.5 \times 10^{-7}$ M O$_2$
(25 ppb), TGSCC, 200°C.
Figure 111

Sensitized Type 304 stainless steel, 200°C, 6.2x10^{-7} M O_2 (20 ppb) (Inlet), TGSCC.
Figures 112-117 illustrate the behavior that was observed for sensitized Type 304 stainless steel when tested at 150°C. Figures 112-115 correspond to samples tested with dissolved oxygen concentrations between 3.1 and 7.55x10^{-6} M (100 and 250 ppb). There is some indication of crack initiation but essentially no crack propagation. When samples were tested at 150°C in water containing 1.55 - 3.1x10^{-7} M O_2 (5-10 ppb O_2) there was some crack propagation (See Figure 116 and 117). The extent of the TGSCC increased as the dissolved oxygen concentration was decreased.

In addition to the crack propagation rate, there are several other parameters used by authors to denote SCC susceptibility in CERT testing. Some of these methods are: Toshiba's cracking index, I\textsubscript{CSRT}; General Electric's cracking index, I\textsubscript{DS}; \sigma\textsubscript{UTS (Environment)}/\sigma\textsubscript{UTS (Air)}; \%Elongation (Environment)/\%Elongation (Air); e\textsubscript{UTS (Environment)}/e\textsubscript{UTS (Air)}; and e\textsubscript{f (Environment)}/e\textsubscript{f (Air)}. A complete discussion of these parameters is given in Appendix A. Basically an increase in SCC susceptibility results in:

1. Increase in I\textsubscript{CSRT}
2. Increase in I\textsubscript{DS}
3. Decrease in \sigma\textsubscript{UTS (Environment)}/\sigma\textsubscript{UTS (Air)}
4. Decrease in \%E (Environment)/\%E (Air)
5. Decrease in e\textsubscript{UTS (Environment)}/e\textsubscript{UTS (Air)}
6. Decrease in e\textsubscript{f (Environment)}/e\textsubscript{f (Air)}

The cracking effect of the dissolved oxygen concentration as a function of various indices is provided in Appendix E.
Sensitized Type 304 stainless steel, 140°C, 6.4x10^{-6} M O_2, (225 ppb) (Inlet)

Sensitized Type 304 stainless steel, 150°C, 7.5x10^{-6} M O_2, (250 ppb) (Inlet)

Sensitized Type 304 stainless steel, 150°C, 4.5x10^{-6} M O_2, (150 ppb) (Outlet)

Sensitized Type 304 stainless steel, 150°C, 4.5x10^{-6} M O_2, (150 ppb) (Inlet)

Figures 112, 113, 114, 115
Sensitized Type 304 stainless steel, 150°C, 3.1x10^{-7} M O_2 (10 ppb)

Figures 116, 117

Sensitized Type 304 stainless steel, 150°C, 3.1x10^{-7} M O_2 (10 ppb)
Regardless which susceptibility parameter is used the results are the same:

(1) At any given oxygen concentration greater than the "threshold" value for that particular test temperature there is a strong temperature dependence of the SCC susceptibility for the sensitized material. The "threshold" oxygen concentrations correspond to the onset of IGSCC and vary from approximately $1.55 \times 10^{-6}$ M (50 ppb) at 290°C to approximately $9.3 \times 10^{-6}$ M (300 ppb) at 200°C.

(2) At oxygen concentrations below the threshold concentrations the sensitized materials fail due to TGSCC.

(3) At all test temperatures the crack propagation rate was independent of the oxygen concentration at oxygen concentrations below the threshold value.

(4) The increase in crack propagation rate observed for sensitized Type 304 stainless steel at all concs. of dissolved oxygen is greater when the temperature is increased from 200°C to 250°C than when the temperature is increased from 250°C to 290°C.

4.4.1.2 Effect of Test Temperature

The effect of test temperature on the SCC susceptibility of Type 304 stainless steel in high temperature, high purity water was studied at oxygen concentrations from $1.55 \times 10^{-7}$ M (5 ppb) to $1 \times 10^{-3}$ M (32 ppm). The test temperatures investigated ranged from 150°C to 290°C. The results of the study are presented in this section.

The SCC susceptibility, expressed as da/dt, is plotted as a function of the reciprocal test temperature at dissolved oxygen concentrations of $1 \times 10^{-3}$ M (32 ppm), $2.5 \times 10^{-4}$ M (8 ppb), and $2.5 \times 10^{-5}$ M (800 ppb)
in Figures 118, 119, and 120 respectively. In order to provide easier comparison of the behavior at various dissolved oxygen concentrations, Figure 121 is presented. This figure combines the data of Figures 118-120 plus data for oxygen concentrations from $1.55 \times 10^{-7}$ to $4.5 \times 10^{-6}$ M (5 ppb to 150 ppb) and also the data for quench annealed material. In addition to these figures the data was further separated into three groups: IGSCC, Dual mode cracking; and TGSCC. This set of data is presented in Figures 122, 123, and 124. The composite plot is shown in Figure 125. The SCC susceptibility as a function of temperature is shown in Figure 125. The SCC susceptibility as a function of temperature is shown in Figure 126.

There are two important points to be noted from this data:

(1) The slope corresponding to the materials undergoing IGSCC is different from that for the material undergoing TGSCC. The corresponding activation energies are 17.7 kcal and 6.8 kcal for IGSCC and TGSCC respectively. This indicates that different mechanisms are operating for the two different modes of cracking.

(2) At temperatures in excess of 250°C the SCC susceptibility is no longer a linear function of $1/T$.

SCC susceptibility, expressed as $I_{CSRT}$, is plotted as a function of the test temperature at oxygen concentrations of $1 \times 10^{-3}$ M (32 ppm), $2.5 \times 10^{-4}$ M (8 ppm), $2.5 \times 10^{-5}$ M (800 ppb), less than $1.5 \times 10^{-5}$ M (400 ppb) but greater than $3.1 \times 10^{-6}$ M (100 ppb), and less than $3.1 \times 10^{-6}$ M (100 ppb) in Appendix F.

As the amount of dissolved oxygen in the water increases, the temperature dependence of the SCC susceptibility increases dramatically.
Estimated Crack Growth Rate vs \( \frac{1}{T} \)
Sensitized 304, 650°C/1 Hour
32 ppm \( O_2 \), \( \varepsilon = 10^{-6} \) /Second

Figure 118
Estimated crack growth rate vs \( \frac{1}{T} \), \( 1 \times 10^{-3} \) \( O_2 \) (32 ppm)
Estimated Crack Growth Rate vs $l/T$

Sensitized 304, 650°C / 1 Hour

$8 \text{ ppm O}_2$, $\dot{\varepsilon} = 10^{-6}/\text{Second}$

Figure 119

Estimated crack growth rate vs $1/T$, $2.5 \times 10^{-6} \text{M O}_2$ (8 ppm)
Estimated Crack Growth Rate vs $1/T$

Sensitized 304, 650°C/1 Hour

800 ppb $O_2$, $\dot{\varepsilon} = 10^{-6}$/Second

Figure 120

Estimated crack growth rate vs $1/T$, $2.5 \times 10^{-5} H_2(800$ ppb $O_2)$
Composite Plot - Estimated Crack Growth Rate vs \(\frac{1}{T}\)

304 Stainless Steel, \(\dot{\varepsilon} = 10^{-6}/\text{Sec.}\)

Figure 121  \(\frac{1}{T} \times 10^3, ^\circ\text{K}^{-1}\)

Composite plot - Estimated crack growth rate vs \(1/T\)
Estimated Crack Growth Rate vs $1/T$
Sensitized 304, 650°C/1 Hour
Intergranular Cracking, $\dot{\varepsilon} = 10^{-6}$/Sec

Figure J22
Estimated crack growth rate vs $1/T$, IGSCC
Estimated Crack Growth Rate vs $1/T$
Sensitized 304, 650°C/1 Hour
Dual Mode Cracking, $\dot{\epsilon} = 10^{-6}$/Sec

Figure 123
Estimated crack growth rate vs $1/T$, Dual mode SCC.
Estimated Crack Growth Rate vs $1/T$
304 Stainless Steel
Transgranular Cracking, $\dot{\varepsilon} = 10^{-6}$/Sec.

Figure 124
Estimated crack growth rate vs $1/T$, TGSCC
Composite Plot - Cracking Zones
Estimated Crack Growth Rate vs $1/T$

Sensitized 304, 650°C/1 Hour

$\dot{\varepsilon} = 10^{-6}$/Second

Figure 125
Composite plot - Cracking zones - Estimated crack growth rate vs $1/T$. 
Composite Plot—Estimated Crack Growth Rate vs Temperature
Sensitized 304, 650°C/1 Hour
\( \dot{\varepsilon} = 10^{-6} / \text{Sec} \)

Figure 126

Composite Plot—Estimated Crack Growth Rate vs Temperature
The greatest increase in influence occurs between \(1.25 \times 10^{-5} \text{M} \text{O}_2\) (400 ppb \(\text{O}_2\)) and \(2.5 \times 10^{-5} \text{M} \text{O}_2\) (800 ppb \(\text{O}_2\)). It is in this range that the fracture mode is changing from transgranular to intergranular.

The influence of temperature on the cracking mode is made clearer by the following figures. Figures 127 and 128 illustrate the worst cases of IGSCC that occurred in the testing program. Figure 127 shows the cracking that occurred at 290\(^\circ\)C with \(1 \times 10^{-3} \text{M} \text{O}_2\) (32 ppm \(\text{O}_2\)) and Figure 128 shows the cracking that occurred at 290\(^\circ\)C with \(2.5 \times 10^{-4} \text{M} \text{O}_2\) (8 ppm \(\text{O}_2\)). In both cases IGSCC is evident over 100% of the fracture surface. This is also true for the specimen shown in Figure 129 which was tested at 250\(^\circ\)C with \(1 \times 10^{-3} \text{M} \text{O}_2\) (32 ppm \(\text{O}_2\)).

The extent of intergranular cracking at \(1.10^{-3} \text{M} \text{O}_2\) (32 ppm \(\text{O}_2\)) begins to decrease at approximately 200\(^\circ\)C as shown by Figure 130. SEM photographs taken at magnifications in excess of 2000x revealed slip traces on the fracture surface of the specimen.

Specimens tested at 150\(^\circ\)C with \(1.10^{-3} \text{M} \text{O}_2\) (32 ppm \(\text{O}_2\)) show no indication of IGSCC (Figure 131). The same behavior is observed with \(2.5 \times 10^{-4} \text{M} \text{O}_2\) (8 ppm \(\text{O}_2\)) (Figure 132).

Figures 128, 133, 134, 135, 136, and 132 depict the temperature dependence of the susceptibility to cracking at \(2.5 \times 10^{-4} \text{M} \text{O}_2\) (8 ppm \(\text{O}_2\)). Comparison of Figure 128 with that of Figures 133 and 134 shows that cracking susceptibility does increase as the temperature is increased at this oxygen concentration. This point was not evident in any of the mechanical property ratios depicting susceptibility to SCC. However, in Figure 81 susceptibility to SCC denoted as \(\text{d}a/\text{d}t\) does indicate that increasing the temperature from 250\(^\circ\)C to 290\(^\circ\)C will increase the cracking
Figure 127 (Top)

Sensitized Type 304 stainless steel, 290°C
$1 \times 10^{-7} \text{M O}_2$ (32 ppm) IGSCC

Figure 128 (Bottom)

Sensitized Type 304 stainless steel, 290°C
$2.5 \times 10^{-4} \text{M O}_2$ (8 ppm), IGSCC
Figure 129

Sensitized Type 304 stainless steel, 250°C
1x10^{-3} M O_2 (32 ppm), IGSCC.
Figure 130

Sensitized Type 304 stainless steel, 200°C
1x10^{-3} M O_2 (32 ppm), IGSCC
Sensitized Type 304 stainless steel, 150°C
$1 \times 10^{-3} \text{ M O}_2$ (32 ppm)

Figures 131, 132

Sensitized Type 304 stainless steel, 150°C
$2.5 \times 10^{-4} \text{ M O}_2$ (8 ppm)
Figure 133

Sensitized Type 304 stainless steel, 250°C, $2.5 \times 10^{-4} \text{M} \text{O}_2$ (8 ppm), IGSCC.
Figure 134

Sensitized Type 304 stainless steel, 250°C, 2.5x10^{-4} M O_2 (8 ppm), IGSCC
propensity.

Figures 135 and 136 show that decreasing the temperature to 200°C with $2.5 \times 10^{-4} M O_2$ (8 ppm $O_2$) further decreases the cracking severity. No cracking was observed at 150°C with $2.5 \times 10^{-4} M O_2$ (8 ppm $O_2$) (Figure 132).

The temperature dependence of cracking susceptibility with dissolved oxygen concentration of $2.5 \times 10^{-4} M O_2$ (800 ppb $O_2$) was investigated. The results are presented in Figures 137, 139 and 140. Decreasing the test temperature reduces the susceptibility to SCC. SEM photographs of samples tested with $2.5 \times 10^{-5} M O_2$ (800 ppb) dissolved $O_2$ show signs of transgranular cracking at the crack tips at the interior of the specimens.

Two examples of TGSCC observed in sensitized Type 304 stainless steel at low oxygen levels are presented in Figures 141 and 142. The sample pictured in Figure 141 was tested at 250°C with $1.05 \times 10^{-6} M O_2$ (35 ppb $O_2$) (inlet) while the specimen pictured in Figure 142 was tested at 175°C with approximately $4.5 \times 10^{-6} M O_2$ (150 ppb $O_2$) (outlet). The TGSCC is more severe at the higher temperature.

The effects of test temperature on the SCC susceptibility of Type 304 stainless steel in high purity water are summarized below:

(1) As the dissolved oxygen concentrations of the water increases, the influence of the test temperature on the SCC behavior of sensitized Type 304 stainless steel increases. The higher the temperature the greater the susceptibility (Figure 126).

(2) At oxygen concentrations in excess of 800 ppb, a 50°C increase in temperature results in approximately a factor of 2 increase in the
Figure 135 (Left)

Figure 136 (Right)

Sensitized Type 304 stainless steel, 200°C, $2.5 \times 10^{-4}$M O₂ (8 ppm), IGSCC.

Sensitized Type 304 stainless steel, 200°C, $2.5 \times 10^{-4}$M O₂ (8 ppm), IGSCC.
Figure 137
Sensitized Type 304 stainless Steel, 250°C, 2.5x10^{-5} M O_2 (800 ppb) Dual mode SCC.

Figure 138
Sensitized Type 304 stainless steel, 250°C, 2.5x10^{-5} M O_2 (800 ppb), IGSCC
Sensitized Type 304 stainless steel, 200°C
$2.5 \times 10^{-5} \text{M} \text{O}_2$ (800 ppb), Dual mode SCC
Figure 141

Sensitized Type 304 stainless steel, 250°C, 1.1x10^{-6} M O_2 (35 ppb) (Inlet), TGSCC
Figure 142

Sensitized Type 304 stainless steel, 175°C, 4.5x10^-6 H2O (150 ppm) (Outlet), TSSCC
crack propagation rate.

(3) At low oxygen concentrations where TGSCC is observed, an increase in temperature results in an increased crack growth rate (Figure 81).

(4) It appears that two different mechanisms are operating for the two different modes of cracking, IGSCC and TGSCC.

(5) At temperatures in excess of 250°C, the 1/T relationship with SCC susceptibility for the specimens which undergo IGSCC is no longer valid.

(6) The activation energy for TGSCC is approximately half that for IGSCC (6.8 kcal versus 17 kcal respectively).

(7) An increase in test temperature results in only an increase in the crack propagation rate for quench annealed Type 304 stainless steel.

4.4.1.3 Effect of Temperature and Oxygen on SCC

Although the separate effects of temperature and dissolved oxygen on SCC susceptibility are certainly important, in actuality the combined effects of test temperature and dissolved oxygen content on SCC susceptibility are required. To accomplish this, all of the test data for sensitized material was plotted on the same graph to yield the 3-D surface shown in Figure 143. The higher the position of the surface within the cube, the greater is the susceptibility of the material to SCC.

The data was also subjected to a multiple linear regression analysis utilizing the Statistical Analysis System and the System 370 computer at the Ohio State University. Several models were used including linear, 2nd order, 3rd order, 4th order, and 5th order. The best fit was with the 3rd order model. The results are given below:
Figure 143
Effect of temperature and dissolved oxygen content on SCC susceptibility - 3D plot.
\[
\log \frac{da}{dt} = -1008.1 + 1314.1 (T) + 47.4 (Ox) - 564.2 (T^2) + 3 (0x^2) - 40.5 (T) (0x) + 80.6 (T^3) + 6.6 (T^2) (0x) - 1 (T) (0x^2) - 0.01 (0x^3)
\]

where \( T = \log \) (Temp°C) 
\( Ox = \log \) (Dissolved Oxygen Conc., ppb) 

The mechanical strength of materials is epitomized by the stress-strain curve, and the toughness or fracture energy is characterized by the area under the curve (20). SCC is known to reduce the required fracture energy. Therefore the smaller the area beneath the load elongation curve, the greater is the susceptibility to SCC. This method of comparison provides a useful means of comparing and ranking various materials and test conditions.

In Figures 144 and 145 the load versus time plots for various tests during the study are presented. Figure 144 illustrates the effect of temperature on the SCC susceptibility at a given oxygen concentration while Figure 144 shows the effect of dissolved oxygen concentration at a fixed temperature.

4.4.1.4 Effect of Strain Rate

The applied strain rate was chosen as a variable for the investigation. Three strain rates were chosen: \( 10^{-6} \)/sec, \( 10^{-5} \)/sec, and \( 10^{-6} \)/sec. At a strain rate of \( 10^{-4} \)/sec no cracking was observed in any test condition. The results for tests employing a strain rate of \( 10^{-5} \)/sec are shown in Figure 146. Cracking susceptibility is denoted by the use of the cracking index developed by Toshiba (See Appendix A for a complete description). The larger the cracking index value the greater the material susceptibility to SCC. The results at a strain rate of \( 10^{-5} \)/sec are compared to those at a strain rate of \( 10^{-6} \)/sec in Figure 147.
Stress vs Time Curves

Effect of Dissolved Oxygen Content on Susceptibility to SCC
304 Stainless Steel, 250°C
\( \dot{\varepsilon} = 10^{-6} \text{ / Sec} \)

Figure 144

Stress versus time curves - Effect of dissolved oxygen content on susceptibility to SCC, 250°C
Stress vs. Time Curves

Effect of Temperature on Susceptibility to SCC

304 Stainless Steel

\[ \dot{e} = 10^6 \text{ / Sec}, 8 \text{ ppm } O_2 \]

Figure 145

Stress versus time curves - Effect of temperature on susceptibility to SCC, 2.5x10^{-4}M O_2 (8 ppm)
Toshiba Cracking Index vs Dissolved Oxygen Content

304 Stainless Steel

\[ \varepsilon = 10^{-5} \text{/ Second} \]

Dissolved Oxygen, ppb

Figure 146

Toshiba cracking index versus dissolved oxygen content, 
\[ 10^{-5} \text{/sec} \]
Composite Plot - Toshiba Cracking Index vs Dissolved Oxygen Content
Strain Rate Effects at 200°C & 250°C
Sensitized 304 - 650°C / 1 Hour

$250°C, \dot{\varepsilon} = 10^{-2}/\text{sec.}$

$200°C, \dot{\varepsilon} = 10^{-6}/\text{sec.}$

$250°C, \dot{\varepsilon} = 10^{-5}/\text{sec.}$

$200°C, \dot{\varepsilon} = 10^{-5}/\text{sec.}$

Figure 147
Composition plot - Toshiba cracking index vs dissolved oxygen content - Strain rate effects at 200°C and 250°C
Cracking susceptibility depends strongly on the strain rate with the greatest susceptibility occurring with the $10^{-6}$/sec strain rate. The strain rate dependence as a function of test temperature is presented in Figure 148.

4.4.2 Quench Annealed Type 304 Stainless Steel

Quench annealed Type 304 stainless steel was subjected to CERT tests in the high purity water. In Figure 81 the result of this investigation can be seen. At 250°C the estimated crack propagation rate is independent of the dissolved oxygen concentration. SEM photographs of the failed specimens are shown in Figures 149-156. Figures 151 and 152 show the fracture surfaces of specimens that failed when in 250°C water containing $2.5 \times 10^{-4}$ M O$_2$ (8 ppm O$_2$). The cracks are small and "thumb nail" shaped. Cracks in specimens tested in 250°C water containing $1.25 \times 10^{-4}$ M O$_2$ (4 ppm O$_2$) and approximately $1.25 \times 10^{-5}$ M O$_2$ (400 ppb O$_2$) show the same type of cracking (Figures 149 and 150). When the oxygen concentration of water is reduced to the concentration of $3.1 \times 10^{-6}$ M (100 ppb) (outlet) and $1.55 \times 10^{-7}$ M (5 ppb) the depth and extent of the transgranular cracking increases (Figures 153, 154, and 155). Figures 155 and 156 compare the effect of temperature on the cracking behavior of quench annealed material when tested with $1.55 \times 10^{-7}$ M (5 ppb O$_2$). Increasing the temperature from 200°C to 250°C increased the susceptibility to cracking.

4.5 Open Circuit Potentials vs Time

The open circuit potentials of the test specimens were measured during the CERT test by using an internal Ag/AgCl reference electrode. Figures 157-160 show the behavior that was observed for the sensitized
Toshiba Cracking Index vs Temperature
Strain Rate Dependence
8 ppm O₂
304 Stainless Steel

\[
\begin{align*}
I_{CSRT} & = 8 \text{ ppm O}_2 \\
& \text{Sen 304, } \dot{\varepsilon} = 10^{-6}/\text{sec.} \\
& \text{QA 304, } \dot{\varepsilon} = 10^{-6}/\text{sec.} \\
& \text{Sen 304, } \dot{\varepsilon} = 10^{-5}/\text{sec.} \\
& \text{QA 304, } \dot{\varepsilon} = 10^{-5}/\text{sec.}
\end{align*}
\]

Figure 148
Toshiba cracking index vs temperature - strain rate dependence - \(2.5 \times 10^{-6} \text{M O}_2\) (8 ppm)
Quench annealed Type 304 stainless steel, 290°C, 1.3x10^-5 M O₂ (400 ppb), TOSCO.

Figures 149, 150, 151, 152

Quench annealed Type 304 stainless steel, 230°C, 2.5x10^-4 M O₂ (4 ppm), interrupted test, TOSCO.

Quench annealed Type 304 stainless steel, 250°C, 2.5x10^-6 M O₂ (8 ppm), TOSCC
Figure 153 (Left) Quench annealed Type 304 stainless steel, 250°C, 3.1x10^-6 M O_2 (100 ppb) (Outlet), TGSCC.

Figure 154 (Right)
Quench annealed Type 304 stainless steel, 250°C, 3.1x10^-6 M O_2 (100 ppb) (Outlet), TGSCC.
Figure 155
Quench annealed Type 304 stainless steel, 250°C, $1.55 \times 10^{-7} \text{M O}_2$ (5 ppb), TGSCC.

Figure 156
Quench annealed Type 304 stainless steel, 200°C, $1.55 \times 10^{-7} \text{M O}_2$ (5 ppb) TGSCC
Open Circuit Potentials vs Time
Intergranular Cracking
Sensitized 304, 650°C / 1 Hour
\( \dot{\varepsilon} = 10^{-6} / \text{Second} \)

Figure 157
Open circuit potentials vs time, IGSCC
Open Circuit Potentials vs Time, Dual Mode Cracking
Sensitized 304, 650°C/1 Hour, $\dot{E} = 10^{-6}$/Second

Figure 158  Open circuit potentials vs time, TGSCC, Dual Mode SCC
Open Circuit Potentials vs Time
Transgranular Cracking
Sensitized 304, 650°C/1 Hour
$\dot{\varepsilon} = 10^{-6}$/Second

Figure 159 Open circuit potentials vs time, TGSCC
Open Circuit Potentials vs Time
Sensitized 304, 650°C / 1 Hour
No Cracking, 150°C, $\dot{E} = 10^{-6}$/Second

Figure 160  Open circuit potential vs time, No cracking
Specimens which failed due to IGSCC had open circuit potentials between 0 and 300 mV_H (Figure 157). The majority of specimens which failed due to TGSCC possessed open circuit potentials between -400 and -600 mV_H. Specimens exhibiting a dual mode of cracking possessed open circuit potentials between 100 and -400 mV_H. Specimens which did not crack at 150°C all maintained open circuit potentials between 100 and 300 mV_H.

Open circuit potentials for quench annealed specimens which underwent TGSCC are presented in Figure 161.

In Figure 162 and 163 the effect of dissolved oxygen on the open circuit potentials of sensitized stainless steel at temperatures of 200 and 250°C respectively. The general trends are the same as those observed by Lee (119). At a given oxygen concentration, an increase in temperature results in a decrease in the open circuit potential. At a given temperature an increase in the dissolved oxygen concentration results in an increase in the open circuit potential of the specimen.

During the EPRI round robin testing program the open circuit potentials were monitored. The results are shown in Figure 164. These potentials lie at the upper range of the group exhibiting IGSCC as shown in Figure 157. This is to be expected because the round robin tests were conducted at 121°C which should result in a higher open circuit potential.

The observations of the experiments incorporating open circuit potential measurement are summarized below:

(1) Open circuit potentials for specimens exhibiting IGSCC, dual mode cracking, and TGSCC fall into these three distinct zones depending
Open Circuit Potentials vs Time
Transgranular Cracking
Quench Annealed 304
\( \dot{\varepsilon} = 10^{-6} \) / Second

Figure 161
Open circuit potential vs. time, TSSCC, Quench annealed 304
Open Circuit Potentials vs Time, Sensitized 304, 650°C/1 Hour, 200°C, $\dot{e} = 10^{-6}$/Second

Figure 162  Open circuit potentials vs time, 200°C
Open Circuit Potentials vs Time

Sensitized 304-650°C / 1 Hour

250°C, $\dot{\varepsilon} = 10^{-6}$/Second

Figure 163
Open circuit potentials vs time, 250°C
Open Circuit Potentials vs Time
EPRI Round Robin Tests
Sensitized 304
121°C, $\dot{\varepsilon} = 10^{-6}$/ Second
8 ppm O$_2$

Figure 164
Open circuit potentials vs time, EPRI round robin tests, 121°C, 2.5x10$^{-4}$ N O$_2$ (8 ppm).
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upon the type of cracking: IGSCC, 0 to +300 mV$_H$; dual mode cracking, 100 to -400 mV$_H$; TGSCC -400 to -600 mV$_H$.

(2) At a given oxygen concentration an increase in temperature results in a decrease in the open circuit potential of the specimen.

(3) At a given temperature an increase in the dissolved oxygen concentration results in an increase in the open circuit potential of the specimen.

4.6 Static Autoclave Tests

In addition to the tests conducted in the refreshed autoclave system, several tests early in the testing program were conducted in 1 gallon static autoclaves. The fractured sensitized specimens tested in this manner are shown in Figures 165, 166, 167, and 168. Generally speaking, the cracking observed in tests conducted in static autoclaves was not as severe as that observed in specimens tested in refreshed autoclave systems utilizing the same test variables of temperature and oxygen. In Figure 169 the fracture surface of a quench annealed specimen is shown. The specimen was tested at 200°C with 6.2x10$^{-6}$ M O$_2$ (20 ppm O$_2$). The specimen failed due to TGSCC. This same behavior was observed in the refreshed autoclave system at 200°C and 2.5x10$^{-4}$ M O$_2$ (8 ppm O$_2$).

4.7 "Pre-Cracked" Specimens

Early in the testing program, a batch of material was sent to the Electric Heat Treating Company for annealing and sensitization. The material was heat treated in high temperature salt baths. After the CERT tests were conducted on these specimens it was discovered that the specimens had undergone intergranular corrosion in the salt baths.
Figure 165

Sensitized Type 304 stainless steel, 250°C, 1.2x10⁻³⁷ N₂ (40 ppm) ICSCC, Static Autoclave test
Figure 166

Sensitized Type 304 stainless steel, 200°C, 6.2x10^-3 M O_2 (20 ppm), IGSCC, Static autoclave test
Figures 167, 168

Sensitized Type 304 stainless steel, 200°C,
$6.2 \times 10^{-4} \text{M} \text{O}_2 (20 \text{ ppm})$, IGSCC, Static autoclave test

Sensitized Type 304 stainless steel, 100°C,
$1.6 \times 10^{-4} \text{M} \text{O}_2 (5 \text{ ppm})$, Static autoclave test
Figure 169

Quench annealed Type 304 stainless steel, 200°C, 2.5x10^{-6} M O_2 (8 ppm O_2), TCSCC, Static autoclave test.
Therefore these specimens, prior to their testing, possessed "pre-cracks". The results of the CERT tests on these materials are shown in Figures 170-175. Figures 170 and 171 were taken of specimens tested at 250°C with $3.1 \times 10^{-6}$ M $O_2$ (100 ppb $O_2$) and $2.5 \times 10^{-4}$ M $O_2$ (8 ppm $O_2$) respectively. The same pattern holds for these specimens as for the non-pre-cracked ones, i.e. intergranular cracking is found at low dissolved oxygen concentrations.

Figure 172 illustrates the cracking observed on a specimen tested at 225°C with $2.5 \times 10^{-4}$ M $O_2$ (8 ppm $O_2$). The cracks are not as deep as those for the specimen tested at 250°C (Figure 171); however, the cracking is deeper than the cracking observed on the specimen tested at 200°C with $2.5 \times 10^{-4}$ M $O_2$ (8 ppm $O_2$) (Figure 173). The specimens tested at 100°C and 150°C with $2.5 \times 10^{-4}$ M $O_2$ (8 ppm $O_2$) did not show any evidence of IGSCC (Figure 174 and 175).

Several samples of quench annealed material were tested containing "pre-cracks". A specimen tested at 225°C with $2.5 \times 10^{-4}$ M $O_2$ (8 ppm $O_2$) showed evidence of transgranular cracking (Figure 175). A specimen tested at the same temperature with approximately $3.1 \times 10^{-6}$ M $O_2$ (100 ppb $O_2$) did not show any TGSCC (Figure 177). Specimens tested at 200°C, 150°C, and 100°C with a dissolved oxygen concentration of $2.5 \times 10^{-4}$ M $O_2$ (8 ppm) are shown in Figures 178, 179, and 180 respectively. Only the specimen tested at 200°C (Figure 178) shows any indication of TGSCC.

Conclusions drawn from the tests on these pre-cracked specimens are:

(1) The temperature dependence of the cracking susceptibility is the same for the "pre-cracked" specimens as for the smooth specimens.
Figures 170, 171

Sensitized Type 304 stainless steel, 250°C, approx.
3.1x10^{-6} M O_2 (100 pph), Salt bath heat treatment

Sensitized Type 304 stainless steel, 225°C,
2.5x10^{-6} M O_2 (8 ppm), Salt bath heat treatment
Figure 172

Sensitized Type 304 stainless steel, 225°C, 2.5x10^-4 M O2 (8 ppm), Salt bath heat treatment
Figure 173

Sensitized Type 304 stainless steel, 700°C,
2.5x10⁻⁵M O₂ (8 ppm), Salt bath heat treatment.
Figure 174, 175

Sensitized Type 304 stainless steel, 150°C, 2.5x10⁻⁴N O₂ (8 ppm), Salt bath heat treatment.

Sensitized Type 304 stainless steel, 100°C, 2.5x10⁻⁴N O₂ (8 ppm), Salt bath heat treatment.
Figures 176, 177

Quench annealed Type 304 stainless steel, 250°C, approx. 3.1x10^{-6} M O_2 (100 ppb), Salt bath heat treatment.

Quench annealed Type 304 stainless steel, 225°C, 2.5x10^{-6} M O_2 (8 ppm), Salt bath heat treatment.
Figure 178

Quench annealed Type 304 stainless steel, 200°C,
$2.5 \times 10^{-4}$ M O$_2$ (8 ppm), Salt bath heat treatment.

Figure 179

Quench annealed Type 304 stainless steel, 150°C,
$2.5 \times 10^{-4}$ M O$_2$ (8 ppm), Salt bath heat treatment.

Figure 180

Quench annealed Type 304 stainless steel, 100°C,
$2.5 \times 10^{-4}$ M O$_2$ (8 ppm), Salt bath heat treatment.
An increase in test temperature results in an increase in cracking susceptibility.

(2) The presence of the "pre-cracks" did not affect the results in an appreciable manner.

4.8 **EPRI Round Robin Tests**

Special specimens were prepared as prescribed by the Electrical Power Research Institute for the round robin tests from the pipe section provided by General Electric. The specimens were heat treated 20 hours at 585°C in air and the tarnish film was not removed. Identical specimens were shipped to the Ohio State University and to General Electric for testing. The test conditions were as follows:

(1) The tarnish was not to be removed.

(2) Test temperature was 121°C. (Battelle also tested at 149°C.)

(3) Environment was 2.5x10^{-4} M O_2 (8 ppm O_2) high purity water.

(Battelle sparged with a mixture of air and nitrogen.)

No evidence of stress corrosion cracking was found on any of the specimens tested by Battelle (99). This result was based upon mechanical properties, SEM, and metallography examinations.

Four specimens supplied by the General Electric Company and machined and heat treated at the Battelle Columbus Laboratories were subjected to CERT tests as described in Section 3.3. SEM photographs of the fractured specimens are shown in Figures 181 and 182. The specimens fractured in an unusual manner with pie shaped areas corresponding to IGSCC located on the fracture surfaces of both specimens. Figure 181 shows the elongated nature of the grains on the fracture surface. Since this elongated grain structure was not normally seen on samples undergoing IGSCC, two additional specimens of this same material were subjected to
Figure 181 Sensitized Type 304 stainless steel, 121°C, 2.5 \times 10^{-4} \text{M} O_2 (8 \text{ ppm}), \text{EPRI round robin test}

Figure 182 Sensitized Type 304 stainless steel, 121°C, 2.5 \times 10^{-4} \text{M} O_2 (8 \text{ ppm}), \text{EPRI round robin test}
interrupted CERT tests in hope of ascertaining the amount of strain prior to crack initiation. Crack initiation occurred somewhere between 5 and 12.3% strain. This value is higher than that obtained for sensitized material tested at 250°C with $2.5 \times 10^{-6} \text{M } O_2$ (8 ppm $O_2$).

The fact that this material cracked intergranularly at 121°C indicates that there is a great deal that still needs to be understood concerning the metallurgical structure of this material as it relates to SCC resistance. No cracking was ever observed in the material supplied by the Viking Steel Company below 150°C. The different SCC behavior of the two materials must be due to the effect of metallurgical structure and composition.
5.0 DISCUSSION OF RESULTS

This section is divided into four subsections. The first subsection considers the mechanisms of crack initiation and crack propagation. The environmental dependencies of SCC are discussed in the second subsection. Methods of reporting CERT data and experimental difficulties are discussed in the remaining two subsections.

5.1 Mechanisms of Crack Initiation and Crack Propagation

When attempting to determine the mechanisms and the various reactions that are occurring, which in turn are causing the stress corrosion cracking of the material, one of the most important points to remember is that the proposed mechanism or mechanisms must explain the experimental observations. With this in mind any proposed mechanism must explain the following:

(1) Sensitized Type 304 stainless steel undergoes IGSCC in high purity water containing high levels of dissolved oxygen. The cracks initiate intergranularly and continue to propagate intergranularly. This occurs at temperatures above 150°C and oxygen concentrations in excess of $2.5 \times 10^{-5} \text{M} \ (800 \text{ ppb})$.

(2) Sensitized Type 304 stainless steel undergoes TGSCC in high purity water containing low concentrations of dissolved oxygen. The cracks initiate transgranularly and propagate transgranularly. This occurs at temperatures of 150°C and above and with oxygen concentrations
less than approximately $3.1 \times 10^{-6}$ M (100 ppb).

(3) At temperatures in excess of 150$^\circ$C and oxygen concentrations between approximately $3.1 \times 10^{-6}$ M (100 ppb) and $2.5 \times 10^{-5}$ M (800 ppb), sensitized Type 304 stainless steel will undergo a dual mode type of SCC in high purity water. The cracks initiate in an intergranular fashion and then eventually change to a transgranular propagation mode.

(4) Quench annealed Type 304 stainless steel undergoes TGSCC in high purity water with less than $3.1 \times 10^{-6}$ M (100 ppb) of dissolved oxygen. The cracks initiate in a transgranular fashion and propagate transgranularly.

(5) Quench annealed Type 304 stainless steel undergoes TGSCC in high purity water containing approximately more than $3.1 \times 10^{-6}$ M (100 ppb) of dissolved oxygen. The cracks initiate in a transgranular fashion and propagate transgranularly. High stresses and strains are required for crack initiation.

(6) An increase in the testing temperature leads to an increase in the observed crack propagation rates.

(7) The crack propagation rates of materials undergoing IGSCC are dependent upon the concentration of dissolved oxygen in the water. The crack propagation rate increases as the dissolved oxygen concentration increases.

(8) The crack propagation rates of materials undergoing TGSCC do not depend upon the dissolved oxygen concentration of the water.

(9) Decreasing the strain rate of the test leads to an increase in SCC susceptibility for the material being tested. Decreasing the applied strain rate increases the crack propagation rate.
5.1.1 Intergranular Stress Corrosion Cracking of Type 304 Stainless Steel in High Purity Water

This section deals with the IGSCC that occurs in sensitized Type 304 stainless steel when tested in high purity water containing more than $2.5 \times 10^{-5}$ M (800 ppb) dissolved oxygen. The section discusses both crack initiation and crack propagation. The test conditions can be summarized as follows:

1. **Material**—Type 304 stainless steel in the sensitized condition (650°C/hr). Regions adjacent to the grain boundaries are depleted in chromium. Sulfur is present in the grain boundaries.

2. **Environment**—High purity water containing more than $2.5 \times 10^{-5}$ M (800 ppb $O_2$) dissolved oxygen; resistivity 3M ohm-cm; pH-neutral.

3. **Stress**—CERT test; increasing stress and strain situation.

The test that will be considered in detail in this explanation is 250°C, $2.5 \times 10^{-4}$ M $O_2$ (8 ppm $O_2$). The open circuit potentials measured under these conditions are shown in Figure 157. The value of the open circuit potential is approximately +100 mV$_H$. This is in excellent agreement with the work of Lee and Indig (119, 63). The potential measured on the straining specimen is slightly lower than that of the stationary specimen. The specimen which is being strained is constantly having fresh material exposed to the solution which disrupts the integrity of the film and therefore leads to a lower open circuit potential.

Point A on Figure 183 indicates the approximate point on the high temperature E-pH diagram that is indicative of the film stability on the surface of the specimen in contact with the high purity water. The open circuit potential of the specimen falls within the boundaries of the region of film stability. Since the open circuit potential lies near to
Figure 183 $E$-pH Fe-Cr-Ni, 250°C, IGSCC (119).
the Ni²⁺/NiO equilibrium potential, if the film were disturbed the repassivation rate would not be rapid. Therefore a film rupture event would result in dissolution of the alloy.

The conditions necessary for stress corrosion cracks to initiate are present:

(1) A susceptible material:

Sentitization of Type 304 stainless steel produces a region adjacent to the grain boundaries of the alloy in which the chromium concentration drops below 5%. Numerous investigators have found that decreasing the chromium concentration of an alloy reduces its ability to repassivate rapidly.

(2) Environment:

As shown by Figure 183, the open circuit potential of Type 304 stainless steel in high purity water lies just within the boundaries of the region of film stability. However, if this equilibrium situation were disturbed dissolution of the alloy would be expected.

(3) Stress:

The CERT test causes failure of the test specimen by straining the specimen at a constant extension rate until failure. This allows fresh alloy to be constantly exposed to the solution.

Intergranular SCC of sensitized Type 304 stainless steel in high purity water can be explained as follows:

(1) Straining of the specimen causes the protective film to be broken. This film rupture event would probably be favored in the chromium depleted regions adjacent to the grain boundaries (3-4% Cr) or at phase inclusions on the surface of the material.
(2) Once the protective film has been broken, the underlying alloy is retarded in the chromium depleted zones and therefore more dissolution of the alloy occurs in the chromium depleted zones than in the bulk of the alloy.

(3) Repetition of this process would eventually lead to the formation of a macroscopic stress corrosion crack.

As the crack grows it becomes more difficult for oxygen to diffuse to the crack tip. This is illustrated by Figure 184 which shows typical intergranular stress corrosion cracks observed during the investigation. The cracks are deep and relatively sharp which makes oxygen diffusion to the crack tip difficult. A reduction in the concentration of dissolved oxygen at the crack tip would tend to make the crack tip more active than the surface of the alloy. As the potential drops the film inherently becomes more unstable and therefore the driving force for SCC would be increased.

Additional reactions which would be expected to be occurring at or near the crack tip are:

\[
\begin{align*}
\text{Ni}^2+ &\rightarrow \text{Ni}^{++} + 2e^- \quad (8) \\
\text{Ni}^{++} + \text{H}_2\text{O} &\rightarrow \text{NiO} + 2\text{H}^+ \quad (9) \\
\text{Fe}^{++} &\rightarrow \text{Fe}^{++} + 2e^- \quad (10) \\
\text{Fe}^{++] + 2\text{H}_2\text{O} &\rightarrow \text{Fe(OH)}_2 + 2\text{H}^+ \quad (11) \\
\text{M} + \text{S} + 2\text{H}_2\text{O} &\rightarrow \text{HS}^- + \text{H}^+ + \text{M(OH)}_2 \quad (12) \\
\text{P} + 2\text{H}_2\text{O} &\rightarrow 1/2 \text{H}_2 + \text{H}^+ + \text{H}_2\text{PO}_2^- \quad (13)
\end{align*}
\]

All of the reactions (8-13) would tend to lower the pH within the crack. The S and P in reactions 12 and 13 are present in the alloy as segregated species. Although there is little doubt that these reactions are occurring, their overall effect is minimal. Gross acidification of the propagating crack would cause the crack to spread laterally and this is not observed. It is well known that sensitized Type 304 stainless
Figure 184
Typical intergranular stress corrosion cracks, photomicrographs
Steel is susceptible to IGSCC in acid solutions at high temperatures (87, 70). The fact that the cracks do not spread laterally indicates that the hydrolysis issue must be a second-order effect.

The entire IGSCC cracking process can be summarized as follows:

1. The combination of applied stress and strain rate results in rupture of the protective oxide film at localized sites.
2. Significant dissolution of the alloy occurs in the chromium depleted zones of the alloy. The film is not protective over basically an iron substrate, which dissolves when stressed and doesn't repassivate as fast as the areas containing chromium.
3. Steps 1 and 2 are repeated.
4. As the crack begins to propagate, oxygen diffusion to the crack tip becomes restricted and the electrochemical potential at the crack tip is therefore reduced.
5. Reactions take place which lower the pH of the solution within the crack (minimal effect).
6. The electrochemical potential and pH at the crack tip are such that the fresh surface which is exposed after film rupture rapidly goes into solution as divalent metallic cations.
7. Intergranular crack propagation occurs.

5.1.2 **Transgranular Stress Corrosion Cracking of Sensitized and Quench Annealed Type 304 Stainless Steel in High Purity Water**

This section deals with the TGSCC that occurs in sensitized as well as quench annealed Type 304 stainless steel when tested in high purity water containing less than approximately $1.55 \times 10^{-6} \text{ M}$ (50 ppb) dissolved oxygen during CERT testing. The test conditions can be summarized as
follows:

(1) Material—Type 304 stainless steel in the sensitized condition (650°C/hr) and quench annealed Type 304 stainless steel. Sulfur is present in the grain boundaries.

(2) Environment—High purity water containing less than approximately $1.55 \times 10^{-6}$M (50 ppb O$_2$); resistivity 3M ohm cm, pH neutral, temperatures in excess of 150°C.

(3) Stress—CERT test; increasing stress and strain situation.

The case considered in detail in this explanation is that for 250°C and $7.5 \times 10^{-7}$ M O$_2$ (25 ppb O$_2$). The open circuit potential of the specimen measured during the CERT test for these conditions is approximately -500 mV$_H$ (See Figure 188). Point T on Figure 185 corresponds to the appropriate potential and pH for this test. It is obvious that the protective film is less stable at the potentials corresponding to TGSCC than at the potentials corresponding to IGSCC (+100 mV$_H$).

The transgranular stress corrosion cracks probably initiate in much the same fashion as do intergranular stress corrosion cracks. The protective films of the alloy is broken and dissolution of the underlying alloy occurs until the alloy can repassivate. The primary difference between intergranular crack initiation and transgranular crack initiation is that the amount of dissolution which occurs following a film rupture event is much less for transgranular cracking than for intergranular cracking. The combination of the neutral solution with the high stress intensity results in a repassivation rate which is rapid but sufficiently sluggish to give transgranular SCC.
Figure 185 Fe-Cr-Ni, 250°C, TGSCC (119).
In rationalizing the crack propagation stage in TGSCC for this system it is first of all necessary to summarize some key experimental observations.

Figures 186 and 187 present some high magnification SEM photographs of the fracture surfaces of specimens which have undergone IGSCC and TGSCC. The photographs show that the TGSCC cracks are propagating discontinuously. The markings perpendicular to the crack propagation direction are assumed to be crack arrest markings. Therefore any theory of the mechanisms involved in TGSCC of Type 304 stainless steel in high purity water must incorporate the idea of discontinuous crack propagation.

The presence of crack arrest markings on the fracture surface can be accounted for in the following manner. Since the corrosion rate at the crack tip is expected to be relatively low when compared to the IGSCC case, then the repassivation rate of the film must be higher. Therefore, between film rupture and subsequent dissolution events, the film should have enough time to repair itself. This repeated rupturing and repair of the protective film could lead to the crack arrest markings.

If a lower dissolution rate at the tip of the crack is assumed, then it follows that fewer $\text{H}^+$ ions are going produced in the crack tip region. The crack tip region would not be expected to acidify. In addition to this argument, at a potential of $-500 \text{ mV}$ and neutral pH (See Figure 185), the potential of the specimen falls below that for hydrogen evolution at a pressure of $\text{H}_2$ of approximately $10^{-3} \text{atm}$. The recombination of $\text{H}^+$ within the crack would also prevent the crack tip region from
Intergranular SCC, High magnification

Figures 186, 187
Transgranular SCC, High magnification.
becoming highly acidic. Although this recombination of H⁺ in the crack
tip region is probably occurring it is not felt that this is leading to
hydrogen embrittlement. The fact that the crack propagation rate for
TGSCC increased with an increase in test temperature does not support a
hydrogen embrittlement argument.

The entire TGSCC cracking process can be summarized as follows:

(1) The combination of applied stress and strain rate results in
rupture of the protective oxide film at localized sites.

(2) A relatively small amount of dissolution occurs prior to re-
passivation (Low current density) (119)

(3) Steps 1 and 2 are repeated.

(4) The combination of a relatively small amount of hydrolysis and
electrochemical potentials below that for hydrogen evolution prevent the
formation of an acid condition with the crack. Therefore rapid crack
propagation is not favored.

(5) Successive film rupture and repassivation events results in
discontinuous crack propagation.

(6) If the solution within the advancing crack is similar to that
of the bulk then the corrosion rate on the surface and within the crack
should be similar. Lateral dissolution of the crack walls is not as
restricted as was the case for IGSCC. This explains the wide-blunted
cracks observed in the materials which underwent TGSCC.

Figure 188 shows several photomicrographs of transgranular stress
corrosion cracks. Comparison of this figure with Figure 198 clearly
shows that there is more lateral dissolution occurring during TGSCC than
during IGSCC.
Figure 108
Typical transgranular stress corrosion cracks, photomicrographs.
5.1.3 Dual Mode Stress Corrosion Cracking of Sensitized Type 304 Stainless Steel in High Purity Water

This section deals with the dual mode stress corrosion cracking that occurs in sensitized Type 304 stainless steel when tested in high purity water containing less than $2.5 \times 10^{-5} \text{O}_2$ (800 ppb O$_2$) but more than about $3.1 \times 10^{-6} \text{M} \text{O}_2$ (100 ppb O$_2$) using the CERT technique. The process of crack initiation is the same as that for IGSCC (Section 5.1.1). The crack propagation stage of SCC for dual mode cracking consists of two segments. Crack propagation is initially intergranular but switches to transgranular in the interior of the specimen.

The intergranular portion of crack propagation is the same as that described in Section 5.1.1 for IGSCC. The sluggish repassivation kinetics of the chromium depleted zone adjacent to the grain boundaries allows dissolution of the alloy to occur between successive film rupture events. Repetition of this process leads to the initiation of an intergranular stress corrosion crack $[(3.1 \times 10^{-6} \text{M} - 2.5 \times 10^{-5} \text{M})(100 - 800 \text{ ppb})]$.

At the intermediate oxygen concentrations, initially the same process of crack propagation is probably occurring for dual mode cracking as in IGSCC. However, there are at least two reasons why the crack propagation mode eventually switches from intergranular to transgranular. One factor involved in the fracture mode transition is the strain rate at the crack tip. General Electric has shown that by increasing the applied strain rate the fracture mode can be changed from intergranular to transgranular. The strain rate is greatest at the tip of the advancing crack, therefore conditions would be favorable for a fracture mode...
transition. Also, as the crack progresses and the potential within the crack continues to drop as a result of the reduced oxygen supply, eventually the potential at the crack tip falls below that required for the recombination of hydrogen ions. When this occurs the pH at the crack tip should begin to increase and the solution should approach neutral pH. When the potential at the crack tip has fallen below that required for hydrogen recombination the solution at the crack tip is essentially the same as that which causes TGSCC in sensitized as well as quench annealed Type 304 stainless steel. The cracking mode therefore switches from IGSCC to TGSCC.

5.1.4 Transgranular Stress Corrosion Cracking of Quench Annealed Type 304 Stainless Steel in High Purity Water Containing Dissolved Oxygen Concentrations in Excess of \(3.1 \times 10^{-6}\) M (100 ppb)

Quench annealed Type 304 stainless steel underwent TGSCC in high purity water at all concentrations of dissolved oxygen tested. However, at dissolved oxygen concentrations in excess of \(3.1 \times 10^{-6}\) M (100 ppb) the amount of strain necessary to initiate TGSCC is approximately 3 times greater than that necessary at dissolved oxygen concentrations below \(3.1 \times 10^{-6}\) M (100 ppb) (See Figure 75). These results are in agreement with those of Vermilyea (123) who also observed TGSCC in highly cold worked material. This observation is probably of little engineering importance because the amount of cold work necessary to initiate TGSCC is approximately 40%.

The work on the effect of cold work on SCC susceptibility can best be summarized by the following statement. As the amount of cold work which the sample is subjected prior to crack initiation increases, the probability of TGSCC rather than IGSCC increases. This is due to the
higher stresses necessary to cause yielding in the cold worked metal.

5.2 Environmental Dependencies of Stress Corrosion Cracking

The three environmental variables of interest in this investigation were temperature, dissolved oxygen concentration, and applied strain rate. The effects of these variables on the stress corrosion cracking susceptibility of Type 304 stainless steel are discussed in this section.

5.2.1 Effect of Temperature on Crack Propagation Rates

The effect of temperature on crack propagation rates is a function of the dissolved oxygen concentration of the water and of the metallurgical condition of the specimen. The first case considered is that of sensitized Type 304 stainless steel tested in water with dissolved oxygen concentrations in excess of \(2.5 \times 10^{-5}\) M (800 ppb). The work of Lee (119) is extremely useful in describing the effects of temperature on the onset of IGSCC.

Comparing Figures 24, 25, 26, and 27 it can be seen that a transpassive peak does not appear until the temperature of 150°C is exceeded. IGSCC of sensitized Type 304 stainless steel was not observed at temperatures below 150°C. Furthermore all specimens showing IGSCC possessed open circuit potentials corresponding to the transpassive regions of Figures 25, 26, and 27. The following can be concluded:

(1) If intergranular stress corrosion crack initiation is going to occur the open circuit potential of the specimen must fall within or near the transpassive region of the anodic polarization curve for the test temperature in question.

(2) Potentiostatic anodic polarization curves predict the observed behavior, i.e., sensitized Type 304 stainless steel does not undergo
IGSCC below 150°C. This statement is true only for the material tested in this investigation. Unexplained compositional and microstructural variations make it possible for cracking to be initiated at temperatures below 150°C.

Increasing the test temperature increased the observed crack propagation rates for specimens undergoing IGSCC. An increase in the test temperature would favor the cathodic kinetics and therefore would be expected to increase the crack propagation rate. Movement of ionic species in solution should also be increased as the temperature is increased which would result in greater corrosion rates and therefore greater crack propagation rates.

Increasing the test temperature also results in an increased crack propagation rate for specimens undergoing TGSCC. The arguments cited for the IGSCC are valid for the TGSCC case also although the magnitude of the increase in the crack propagation rate is not as great.

The effects of temperature on dual mode SCC are twofold. Their effects on the crack initiation stage of SCC are the same as those for IGSCC (Section 5.1.1). In addition, the temperature of the water influences the stage of cracking during which the cracking mode changes. The oxygen concentration corresponding to the end of dual mode SCC and the onset of TGSCC decreases as the test temperature is increased. Based on high temperature E-PH diagrams, an increase in temperature at a specific oxygen concentration should result in an earlier IGSCC to TGSCC transition.

The data accumulated in this testing program was subjected to a multiple linear regression analysis. The analysis was performed by the
System 370 computer system at the Ohio State University using the Statistical Analysis System. The results are presented in Section 4.7. The best fit was obtained using the following equation:

$$\log \frac{da}{dt} = A + B(T) + C(Ox) + D(T^2) + E(Ox^2) + F(T)(Ox) + G(T^3) + H(T^2)(Ox)$$

$$+ I(T)(Ox^2) + J(Ox^3)$$

where $T = \log \text{(Temp. °C)}$

$Ox = \log(\text{Dissolved Oxygen Cond., ppb})$

This regression analysis was performed for only one heat of material and one sensitization condition. Ideally the crack propagation rate should be expressed as a function of sensitization condition, test temperature, dissolved oxygen content, pH, conductivity, composition, segregation of minor elements, strain rate, etc.

At the present time it is impossible to include all of the variables mentioned above in the regression equation. The next addition to the regression equation will probably be the influence of sensitization condition. General Electric is doing work in this area. By assigning each specimen a number determined in the EPR test denoting degree of sensitization and then assigning the same material a number, I_{DS}, denoting susceptibility to SCC, a correlation between degree of sensitization and susceptibility to SCC can be obtained. With this information at various temperatures and oxygen concentrations the coefficients in equation 18 could be modified to be functions of test temperature, dissolved oxygen concentration, time and temperature of sensitization, alloy composition, and degree of minor element segregation.

The effect of temperature on the SCC susceptibility of Type 304 stainless steel in high purity water can be readily determined by
differentiating Equation 14 with respect to temperature. Equation 15 results.
\[
\frac{d \log da/dt}{dT} = 1314.1 - 1128.4T - 40.5(0x) + 241.8T^2 + 17.2(T)(0x) - 1(0x)^2
\]
(15)

Comparing Equation 15 with Equation 16, which gives the partial derivative of the \( \log da/dt \) with respect to the dissolved oxygen concentration, shows that the temperature exerts a much stronger influence on the crack propagation rate than the dissolved oxygen concentration.
\[
\frac{d(\log da/dt/d0_x)}{d0_x} = 47.4 + 0.6(0x) - 40.5T + 8.6T^2 - 0.2T(0x) - 0.03(0x)^2
\]
(16)

5.2.2 Effect of the Dissolved Oxygen Concentration on Crack Propagation Rates

The effect of the dissolved oxygen concentration on crack propagation rates is a function of the test temperature and the metallurgical condition of the specimen. For specimens undergoing IGSCC an increase in the dissolved oxygen concentration of the water results in an increased crack propagation rate. For specimens undergoing TGGSCC, increasing the dissolved oxygen concentration does not increase the crack propagation rate.

The role of dissolved oxygen in the IGSCC process is to elevate the potential of the specimen into the transpassive region. Further support for this argument concerning the effect of the dissolved oxygen in the water has been given by Lee (119) (Figure 28). This figure shows the effect of dissolved oxygen on the cathodic kinetics of the system. Increasing the dissolved oxygen concentration leads to an increase in the open circuit potential of the specimen. Eventually the open circuit potential falls within the transpassive region on the polarization curve.
IGSCC is only observed when the potential of the specimen lies within the transpassive region. This is necessary because at lower potentials within the passive region the amount of dissolution which occurs between each film rupture event is not sufficient to lead to IGSCC. The current densities necessary for significant dissolution of material to occur following a film rupture event are only found when the potential of the alloy is in the transpassive region. The crack propagation rate of the material undergoing TGSCC is not affected by the dissolved oxygen concentration of the water. A possible reason for this is that once the open circuit potential of the test specimen drops below the value required for the recombination of hydrogen to be favored, the amount of dissolved oxygen present in the water, if it is below the threshold concentration for the onset of TGSCC, does not affect the corrosion kinetics, and therefore the crack propagation rate is independent of the dissolved oxygen concentration of the water.

Multiple linear regression analysis of the test data resulted in the equation shown in Section 4.4.1.3. Differentiating this equation with respect to the dissolved oxygen concentration gives:

\[
d(\log \frac{da}{dt})/d(ox) = 47.4 + 0.6(ox) - 40.5T + 8.6T^2 - 0.2T(0x) - 0.03(0x^2) \quad (17)
\]

Comparisons of this equation (17) with equation 15 reveal the rather strong dependence of the crack propagation rate and much smaller dependence on the dissolved oxygen concentration.

5.2.3 Effect of Strain Rate

The applied strain rate of the CERT test was also a variable in the investigation. The results of this portion of the test are inconclusive. The reason for this is that all of the specimens tested at a strain rate of \(10^{-5}/\text{sec}\) were tested in the beginning of the
investigation. Most of these samples had different heat treating procedures than the samples used for the bulk of the investigation. In spite of this fact the results are shown in Figure 189. It appears that the crack propagation rates for the specimens tested using a strain rate of $10^{-5}$/sec are lower than those of specimens tested at $10^{-6}$/sec. However, the credibility of such a conclusion is questionable due to the scatter in the data and the heat treatment problems alluded to previously.

In addition to Figure 189, Figure 147 also illustrates the effect of strain rate on the SCC susceptibility of the material. The effect of strain rate is more pronounced when plotted in this manner.

5.3 Methods of Reporting CERT Data

At the present time there is no method of reporting data generated during CERT testing which is recognized as the best characterization of SCC susceptibility. The various methods of reporting the data can be grouped into five categories:

(a) Ratios of mechanical properties—\(\sigma_{\text{UTS (Envir)}}/\sigma_{\text{UTS (Air)}}\), \(e_{T(\text{Envir})}/e_{T(\text{Air})}\), \(e_{UTS(\text{Envir})}/e_{UTS(\text{Air})}\), \(zE(\text{Envir})/zE(\text{Air})\), \(zR.A.(\text{Envir})/zR.A.(\text{Air})\), TFS(Envir)/TFS(Air), etc.

(b) Combination of mechanical properties—Cracking indexes—ICRST, \(I_{DS}\) (See Appendix A).

(c) Visual and optical microscopy

(d) Scanning electron microscopy

(e) Crack propagation rate

The final determination as to whether or not a specimen had undergone SCC is usually made based upon either optical microscopy or SEM.
Figure 189. Effect of strain rate on crack propagation rates

$O_2 > 2.5 \times 10^{-14} M (60 \text{ppm})$
Therefore any method of analyzing the data which utilizes either of these methods should be inherently more precise. Estimated crack propagation rates determined through the use of SEM should therefore be a reliable means of assessing a material's resistance to SCC. In addition, determination of an estimated crack growth rate provides useful engineering data which can be used by design engineers.

An interesting example of the accuracy of the estimated crack growth rate parameter as a method of reporting CERT results is provided in Section 4.0. When comparing the test results at 250°C with those at 290°C, examination of Figures 190 through 195 (Appendix E and F) indicates that sensitized Type 304 stainless steel is more susceptible to IGSCC at 250°C than at 290°C. However, SEM photographs clearly indicate that SCC was more severe at 290°C than at 250°C for these materials (Figures 127, 129, and 134). Examination of Figure 81 reveals that the estimated crack growth rate parameter ranks these tests properly.

In actuality the data obtained in CERT tests should be plotted several different ways in order to obtain the greatest amount of information about a particular specimen in the chosen environment. Plotting of the estimated crack growth rate and a cracking index as a function of the various test variables is recommended.

5.4 Experimental Difficulties

The primary experimental difficulties fall into three categories: load measurement, potential measurement, and oxygen consumption in the autoclave system. These problems are described in the following three sections.
5.4.1 Load Measurement

The only problem associated with the measurement of the load on the specimen was the determination of the effect of the Teflon gland in the Conax fitting on the frictional resistance of the pull rod. This frictional resistance is a function of the test temperature and the test pressure. This frictional resistance was less than 5% and usually about 2% of the maximum load. The accurate measurement of this load was not possible. The values obtained from test to test were not easily comparable. For this reason the load correction due to friction has been neglected. The primary means of comparing the results of the various CERT tests in this investigation is the estimated crack growth rate. The decision to neglect the friction correction does not affect the estimated crack growth rate prediction.

5.4.2 Measurement of the Specimens' Open Circuit Potential

Electrochemical measurements at elevated temperatures have been made possible through the development of reference electrodes which are usable at temperatures up to 300°C. The particular reference electrode used in this study has been described elsewhere by Agrowal and Staehle (116). This reference electrode was reliable at temperatures up to 250°C for approximately one week. For the tests conducted at 290°C the Ag/AgCl reference electrode became unstable after one day. A reference electrode was needed that would remain stable at 290°C for approximately one week. A platinum wire was used as the reference electrode for all tests conducted at 290°C. The work of Lee (119) made it possible to determine the potential of the 304 stainless steel samples with respect to the hydrogen electrode from the measured potentials with respect to the
platinum electrode.

A reoccurring problem which plagued the experimental program was the occasional loss of the electrical isolation of the test specimen. The specimen was isolated from the autoclave as shown in Figures 52 and 56. Most of the isolation problems occurred at the joint shown in Figure 57. Oil leakage from the gear reduction units occasionally leads to a short circuit in this joint. If this short circuit occurred, the experiment was not invalidated; however, the open circuit potential as a response was useless.

5.4.3 Consumption of Oxygen Within the Refreshed Autoclave System

The greatest problem encountered during the testing program was the determination and control of the dissolved oxygen concentration within the autoclave. The control of the dissolved oxygen concentration entering the autoclave was accomplished through the use of a gas proportioner and automated control equipment. These controls allowed excellent control of the dissolved oxygen concentration entering the pressurized portion of the refreshed autoclave system.

The main problem concerning control of the dissolved oxygen concentration of the system occurs within the pressurized portion of the refreshed autoclave system. At elevated temperatures, 200, 250 and 290°C, General Electric has discovered that appreciable oxygen consumption takes place within the system due to oxidation of the autoclave and piping. At oxygen concentrations in excess of $2.5 \times 10^{-5} M$ (800 ppb) this consumption problem becomes a major issue. This fact is illustrated by comparing Figure 23 with Figure 21. Indig et al. (63) at General Electric obtained Figure 23 using a titanium refreshed autoclave system which
minimized the amount of oxygen consumption occurring in the system. Note that all of the potentials obtained in the range of $1.55 \times 10^{-6} \text{M}$ (50 ppb) to $2.5 \times 10^{-5} \text{M}$ (800 ppb $\text{O}_2$) are higher than those measured by Lee in an Inconel 600 autoclave (Figure 21). The potentials measured in the titanium autoclave at extremely low oxygen concentrations are also lower than those obtained in the Inconel 600 autoclave. The reason for this is not known.

The autoclave system used in this investigation was made entirely of Type 316 stainless steel. The oxygen consumption problem during testing was therefore present. The only way to handle this problem was to measure the inlet and outlet oxygen concentrations and plot the data as a function of both values. In the future, testing should be carried out in titanium refreshed autoclave systems in order to minimize this problem.
6.0 SUMMARY AND CONCLUSIONS

Type 304 Stainless steel will undergo SCC in high purity water, at temperatures in excess of 150°C, with dissolved oxygen concentrations between $1.55 \times 10^{-7} \text{M} \, (5 \text{ ppb})$ and $1 \times 10^{-3} \text{M} \, (32 \text{ ppm})$. The important findings of the investigation are listed below:

(1) Sensitized Type 304 stainless steel undergoes IGSCC in high purity water containing high concentrations of dissolved oxygen. The cracks initiate intergranularly and continue to propagate intergranularly. IGSCC occurs at temperatures above 150°C with oxygen concentrations in excess of $2.5 \times 10^{-5} \text{M} \, (800 \text{ ppb})$.

(2) Sensitized Type 304 stainless steel undergoes TGSCC in high purity water containing low concentrations of dissolved oxygen. The cracks initiate transgranularly and crack propagation is transgranular. This occurs at temperatures of 150°C and above with oxygen concentrations approximately less than $3.1 \times 10^{-6} \text{M} \, (100 \text{ ppb})$.

(3) At temperatures in excess of 150°C with oxygen concentrations approximately $3.1 \times 10^{-6} \text{M} \, (100 \text{ ppb})$ and $2.5 \times 10^{-5} \text{M} \, (800 \text{ ppb})$, sensitized Type 304 stainless steel will undergo a dual mode of SCC in high purity water. The cracks initiate in an intergranular fashion and eventually switch to a transgranular propagation mode.

(4) Quench annealed Type 304 stainless steel undergoes TGSCC in high purity water containing less than $3.1 \times 10^{-6} \text{M} \, (100 \text{ ppb}) \, O_2$ at
temperatures in excess of 150°C. The cracks initiate in a transgranular fashion and propagate transgranularly.

(5) Quench annealed Type 304 stainless steel will undergo TGSCC in high purity water containing approximately more than \(3.1 \times 10^{-6}\) M \(O_2\) (100 ppb \(O_2\)) at temperatures in excess of 150°C. The cracks initiate in a transgranular fashion and propagate transgranularly. High strains are required for crack initiation.

(6) An increase in the test temperature leads to an increase in the observed crack propagation rate.

(7) The crack propagation rates of materials undergoing IGSCC are dependent upon the concentration of dissolved oxygen in the water. The crack propagation rate increases as the dissolved oxygen concentration of the water increases at a given temperature.

(8) The crack propagation rates of materials undergoing TGSCC are not dependent upon the dissolved oxygen concentration of the water.

(9) Decreasing the strain rate from \(10^{-5}/\text{sec}\) to \(10^{-6}/\text{sec}\) leads to an increase in the SCC susceptibility of the material being tested.

(10) The open circuit potentials of specimens undergoing IGSCC fall between 0 and +300 mV\(_H\). This potential range corresponds to the transpassive region of the anodic polarization curve.

(11) The open circuit potentials of specimens undergoing TGSCC fall between -400 and -600 mV\(_H\). This potential range corresponds to a secondary peak on the anodic polarization curve denoting film instability.

(12) The open circuit potentials of the specimens undergoing dual mode SCC fall between 0 and -400 mV\(_H\).
(13) Specimens showing IGSCC undergo crack initiation at approximately 6% total strain.
(14) Specimens showing TGSCC undergo crack initiation at approximately 9% total strain.
(15) Quench annealed Type 304 stainless steel at high oxygen concentrations undergoes crack initiation at approximately 25% total strain.
(16) As the test temperature increases, the oxygen concentration at which TGSCC begins decreases.
(17) The estimated crack propagation rates for IGSCC and TGSCC follow a 1/T relationship up to 250°C. Above 250°C deviation in the 1/T relationship appears to be occurring.
(18) The activation energy for TGSCC is approximately half that of IGSCC; 6.8 kcal vs. 17.7 kcal respectively.
(19) The proposed crack initiation process for IGSCC in sensitized Type 304 stainless steel is localized dissolution of the substrate following a film rupture event. The sluggish repassivation kinetics of the chromium depleted zones adjacent to the grain boundaries allows significant dissolution of the substrate to occur prior to repassivation. This results in crack initiation.
(20) IGSCC crack propagation in sensitized Type 304 stainless steel results from the repetition of the process described in #19 above. In addition, as the crack progresses it becomes increasingly more difficult for oxygen to diffuse to the crack tip, which in turn lowers the potential of the material at the crack tip. Also as material goes into solution, hydrolysis of the cations takes place which results
in some localized acidification. Both the potential drop and the acidification would facilitate crack propagation.

(21) The proposed crack initiation process for TGSCC in sensitized Type 304 stainless steel is localized dissolution of the substrate following a film rupture event. The relatively rapid repassivation rate of the material in the neutral solution prevents rapid crack propagation but the repassivation rate is sufficiently sluggish to result in TGSCC. Crack initiation and propagation is transgranular due to the high stresses present during the test.

(22) The fracture mode transition which occurs in sensitized Type 304 stainless steel when it is tested in high purity water containing approximately $3\times10^{-6}$ M $O_2$ (100 ppb $O_2$) to $2.5\times10^{-5}$ M $O_2$ (800 ppb $O_2$) may occur when:

(a) the potential at the crack tip falls below that required for hydrogen recombination or
(b) the strain rate at the crack exceeds a critical value or
(c) the stress intensity at the crack tip exceeds some critical value.

(23) TGSCC of quench annealed Type 304 stainless steel apparently does not occur until the material has been cold worked.

In addition to the conclusion drawn from this investigation, during the testing, several suggestions for areas which require further investigation were developed:

(1) The EPRI round robin tests indicate the importance of the material composition and heat treatment on the SCC susceptibility of these materials. This area needs investigation so that the results of this investigation can be extended to other heats of Type 304 stainless steel
and the various heat treatments.

(2) The entire area of corrosion fatigue resistance of Type 304 stainless steel in high temperature, high purity water has not been investigated. The early indications are that this material is highly susceptible.

(3) The effects of solution conductivity, pH, and applied potential on the SCC susceptibility of Type 304 stainless steel in high temperature, high purity water need to be determined.

(4) Future tests should be conducted in a titanium refreshed autoclave system so that reliable measurement of the dissolved oxygen concentration within the autoclave can be made.
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APPENDIX A

Data obtained in CERT tests can be evaluated in many ways. The most popular methods of evaluation involve ratios of mechanical properties and combinations of these ratios. The two ratio combination or cracking indexes used in reporting the data generated in this investigation are called the General Electric Cracking Index and the Toshiba Cracking Index.

G.E. Cracking Index

\[
I_{DS} = 1 - \frac{C^1_W(1-E_W)}{C^1_a(1-E_a)}
\]

Toshiba Cracking Index

\[
I_{CRST} = 1 - \frac{(C^1 x E)_W}{(C^1 x E)_a}
\]

\(C^1_W\) - Maximum Stress in Oxygenated Water

\(C^1_a\) - Maximum Stress in Air

\(E_W\) - %Elongation in Oxygenated Water

\(E_a\) - %Elongation in Air
APPENDIX B

The following discussion is a brief description of the procedures that are followed in developing high temperature E-pH diagrams. The procedure has been described in detail elsewhere (155, 156, 157).

By using the relation \( \Delta F^o = -nF \theta \), the standard electrode potential of any half-cell reaction at any temperature \( T \) can be referred to its standard value at 25°C by the use of

\[
\Delta F^o_{T2} = \Delta F^o_{T1} + \int_{T1}^{T2} \Delta CpdT - T_2 \int_{T1}^{T2} \Delta C_p/T dT - \Delta T \Delta S^o_{T1}
\]

Unfortunately the \( C_p \) data are not available for most ionic species. However Criss and Cobble (152, 153) have devised a theoretical method for solving the equation for \( \Delta F^o_{T2} \) using what is referred to as the Correspondence Theory of Ionic Entropy". In their theory they use what they call the Correspondence Principle of Ionic Entropy:

\[
S^o_{T2} (\text{abs}) = a(T_2) + b(T_2) S^o_{25} (\text{abs})
\]

The Correspondence Principle does have theoretical justification, and the papers by Criss and Cobble provide the necessary values for the coefficients.

To calculate values of \( \Delta F^o_{T2} \) using the Correspondence Principle it is convenient following Criss and Cobble, to use the following definitions:

\[
\overline{C_p} \bigg|_{T_1}^{T_2} = \text{average value of the heat capacity}
\]

\[
\overline{C_p} \bigg|_{T_1}^{T_2} = \int_{T_1}^{T_2} \overline{C_p} dT = \int_{T_1}^{T_2} Cpd\ln T
\]

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Therefore $\Delta F^o_T = \Delta F^o_{T_1} - \Delta T \Delta S^o_{T_1} + \overline{Cp} \bigg|^{T_2}_{T_1} \left[ \Delta T \Delta S^o_{T_2} \ln \frac{T_2}{T_1} \right]$.

$\overline{Cp} \bigg|^{T_2}_{T_1}$ is calculated from the entropy data of Criss and Cobble by the following relation:

$$\overline{Cp} \bigg|^{T_2}_{T_1} = \frac{S^o(T_2) - S^o(T_1)}{\ln \left( \frac{T_2}{T_1} \right)}$$

The values obtained for $\Delta F^o_T$ are converted to $E^o_T$ values using the relationship:

$$E^o_T = \frac{-1}{nF} \Delta F^o_T$$
APPENDIX C

The constant extension rate equipment consists of a variable speed electric motor, a 900:1 rear reducer, a variable ratio gear reducer, a worm reduction gear (60:1), and a threaded shaft (18 threads/in). With this equipment the extension rates can be varied from 5x10^-7 in/sec to 5x10^-5 in/sec. A sample strain rate calculation is shown below.

<table>
<thead>
<tr>
<th>Motor Speed Reduction Variable Ratio Gear Reducer Worm Gear</th>
<th>Gear</th>
<th>Reducer</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Rev/Min) x (16/12) x (1/30) x (1/900) x (1/60)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Threaded Shaft 1 min/60sec 1/Gauge Length of Sample
x (1/18) x (1/60) x (1/.5) = Strain Rate (in/in sec)

A motor speed of 656 RPM yields a strain rate of 1x10^-6 in/sec.
APPENDIX D

The calculation of the dissolved oxygen content of the water in the static autoclave at elevated temperature and pressure is shown below for a 1 gallon autoclave and a test temperature of 286°C (*).

The value ratio of water and air in the autoclave is 3:2, and water contains 7 ppm dissolved oxygen at the beginning of the experiment. Therefore the total weight of oxygen in the autoclave is:

\[
3000 \text{ (g)} \times (7 \times 10^{-6}) + 2(1) \times 0.21 \times 273 / 293 \times 32 / 224 \text{ g mol/l mol} = 0.58 \text{g}
\]

The volume of water after heating to 286°C is:

\[
3000 \text{ (g)} \times 1.37 \times (1 - 50 \times 10^{-6} \times 71) = 4100 \text{ (ml)}\]

where 1.37 = specific volume ratio of water at 286°C (ml/g), 50 \times 10^{-6} is the compressive volume constant of water at 286°C (L/kg/cm²), and 71 = saturated vapor pressure at 286°C, (kg/cm²)

Water can contain 0.56 ml O₂/g H₂O (800 ppm) at 286°C under an oxygen pressure of 7.1 kg/cm. In the case of deareated water, placing CO₂ (ppm) for the oxygen concentration at 286°C, the total oxygen balance in the autoclave is expressed by:

\[
3000 \times CO₂ \times 10^{-6} + (5 - 4.1) \times CO₂ / 800 \times 7.1 / 1.03 \times 273 / 559 \times 32 / 22.4 = 0.58
\]

Therefore, CO₂ = 69 ppm.

* Private communication with M. Hishida
APPENDIX E

Effect of the dissolved oxygen concentration at various temperatures on the SCC susceptibility of Type 304 stainless steel in high temperature-high purity water. Parameters used to denote susceptibility to SCC are; $I_{CSRT}$, $I_{DS}$, $\sigma_{UTS}^{\text{Environment}}/\sigma_{UTS}^{\text{Air}}$, $\%E^{\text{Environment}}/\%E^{\text{Air}}$, $\varepsilon_{UTS}^{\text{Environment}}/\varepsilon_{UTS}^{\text{Air}}$, $e_f^{\text{Environment}}/e_f^{\text{Air}}$ at $E = 10^{-6}/\text{sec}$, $e_f^{\text{Environment}}/e_f^{\text{Air}}$ at $E = 10^{-5}/\text{sec}$. 
Figure 190  Toshiba cracking index versus dissolved oxygen content

Toshiba Cracking Index vs Dissolved Oxygen Content
304 Stainless Steel, $\varepsilon = 10^{-6}$/Second

- Sen 304, 290°C
- QA 304, 290°C
- Sen 304, 250°C
- QA 304, 250°C
- Sen 304, 225°C
- QA 304, 225°C

Dissolved Oxygen, ppb

I_{CSRT}
General Electric's Cracking Index vs Dissolved Oxygen Content
304 Stainless Steel, $\dot{\varepsilon} = 10^{-6}$/Second

Figure 191 General Electric's cracking index vs dissolved oxygen content
Figure 192 \( \frac{\sigma_{\text{UTS (environment)}}}{\sigma_{\text{UTS (air)}}} \) vs dissolved oxygen content

\( \sigma_{\text{UTS (environment)}}/\sigma_{\text{UTS (air)}} \) vs Dissolved Oxygen Content

304 Stainless Steel \( \varepsilon = 10^{-6} \) / Second

- 250°C QA
- 290°C Sen
- 200°C Sen

- Sen 304, 290°C
- Sen 304, 200°C
- Sen 304, 250°C
- Sen 304, 175°C
- QA 304, 250°C
- QA 304, 175°C
- Sen 304, 225°C
- Sen 304, 150°C
- QA 304, 225°C
- QA 304, 150°C

Dissolved Oxygen, ppb

Figure 192 \( \sigma_{\text{UTS (environment)}}/\sigma_{\text{UTS (air)}} \) vs dissolved oxygen content
Figure 19.3  % Elongation (environment)/% Elongation (air) vs dissolved oxygen content
Figure 194 - $\frac{\varepsilon_{\text{UTS (environment)}}}{\varepsilon_{\text{UTS (air)}}}$ versus dissolved oxygen content

- $\varepsilon_{\text{UTS (environment)}}$ and $\varepsilon_{\text{UTS (air)}}$ are the UTS (ultimate tensile strength) under environmental and air conditions, respectively.

- The graph shows the relationship between dissolved oxygen content (ppb) and the ratio of UTS under environmental conditions to UTS under air conditions for 304 Stainless Steel.

- The data points are labeled with symbols corresponding to different temperatures and conditions:
  - Sen 304, 290°C
  - QA 304, 290°C
  - Sen 304, 200°C
  - QA 304, 200°C
  - Sen 304, 250°C
  - QA 304, 250°C
  - Sen 304, 175°C
  - QA 304, 175°C
  - Sen 304, 150°C
  - QA 304, 150°C
  - Sen 304, 225°C
  - QA 304, 225°C

- The graph illustrates how the ratio of UTS changes with dissolved oxygen content at various temperatures.

- The figure highlights the effect of oxygen on the UTS of 304 Stainless Steel under different environmental conditions.

- The y-axis represents the ratio of UTS under environmental to air conditions, while the x-axis shows the dissolved oxygen content in ppb.
Figure 195  $\frac{e_f(\text{environment})}{e_f(\text{air})}$ versus dissolved oxygen content, $\dot{\varepsilon} = 10^{-6}$ /sec
Figure 196  $\frac{e_f(\text{environment})}{e_f(\text{air})}$ versus dissolved oxygen content

304 Stainless Steel

$\dot{\varepsilon} = 10^{-5}$/Second

- $\Delta$ Sen 304, 250°C
- $\Diamond$ Sen 304, 150°C
- $\bigcirc$ QA 304, 250°C
- $\blacksquare$ QA 304, 150°C
- $\blacktriangle$ Sen 304, 225°C
- $\blacklozenge$ Sen 304, 100°C
- $\bullet$ QA 304, 225°C
- $\blacklozenge$ QA 304, 100°C
- $\blacktriangledown$ Sen 304, 200°C
- $\blacklozenge$ QA 304, 200°C

Dissolved Oxygen, ppb

$e_f(\text{environment})/e_f(\text{air})$ vs Dissolved Oxygen Content
APPENDIX F

The effect of temperature on the SCC susceptibility of Type 304 stainless steel in high temperature-high purity water is compared at various dissolved oxygen concentrations. The parameter used for comparison is the Toshiba Cracking Index.
Toshiba Cracking Index vs Temperature
32 ppm O₂
304 Stainless Steel

Figure 157 Toshiba cracking index vs. temperature, $1 \times 10^{-3} \cdot 10^3 (32 \text{ ppm})$
Figure 190. Toshiba Cracking Index vs. Temperature, 8 ppm O₂

Toshiba Cracking Index vs Temperature
8 ppm O₂
304 Stainless Steel

- Sen 304, \( \dot{\varepsilon} = 10^5 \text{/sec.} \)
- QA 304, \( \dot{\varepsilon} = 10^6 \text{/sec.} \)

Figure 190: Toshiba cracking index vs. temperature, 8 ppm O₂ (8 ppm)
Figure 199  Toshiba cracking index vs. temperature, $2.5 \times 10^{-5}$ mol $O_2$ (800 ppb)
Toshiba Cracking Index vs Temperature

400 ppb > O₂ > 100 ppb

304 Stainless Steel

△ Sen 304, \( \dot{\varepsilon} = 10^6/\text{sec.} \)

▲ QA 304, \( \dot{\varepsilon} = 10^6/\text{sec.} \)

Figure 200  Toshiba cracking index vs. temperature, \(1.25 \times 10^{-5} \text{M} \) O₂ (400 ppb)

\( \text{O}_2 \) 3.1 \( \times 10^{-6} \text{M} \) O₂ (100 ppb)
Toshiba Cracking Index vs Temperature
$O_2 < 100 \text{ ppb}$
304 Stainless Steel

$\Delta$ Sen 304, $\dot{\varepsilon} = 10^6/\text{sec.}$
$\blacktriangle$ QA 304, $\dot{\varepsilon} = 10^6/\text{sec.}$

Figure 201 Toshiba cracking index vs. temperature, $3.1 \times 10^{-6} \text{ ppt} O_2 (100 \text{ ppb})$
Composite Plot - Toshiba Cracking Index vs Temperature - $\dot{\varepsilon} = 10^{-6}$/Second

Sensitized 304-650°C/1 Hour

- 8 ppm O$_2$
- 32 ppm O$_2$
- 800 ppb O$_2$
- 100 ppb O$_2 < O_2 < 400$ ppb O$_2$
- O$_2 < 100$ ppb

Figure 202

Composite plot-Toshiba cracking index vs. temperature, strain rate=$10^{-6}$/sec.