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CORROSION AND STRESS CORROSION CRACKING OF TYPE 304 STAINLESS STEEL AND CARBON STEEL IN SIMULATED BOILING WATER REACTOR

The Ohio State University

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CORROSION AND STRESS CORROSION CRACKING OF
TYPE 304 STAINLESS STEEL AND CARBON
STEEL IN SIMULATED BOILING WATER REACTOR

DISSERTATION

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

By

Ho Jin Choi, B.S.Met. Engr

The Ohio State University

1981

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"And without faith it is impossible to please God, because who comes to him must believe that he exists and that he rewards those who earnestly seek him" (Heb. 11:6)

This dissertation is dedicated to my entire family. To my parents, Charlie, J.J., M.J., M.H.J., and D.Y. who enabled me to attend college. To my loving wife Un Sook (Hanna), whose patient prayer, support and encouragement make it all possible. To my courageous brothers and sisters in Christ, whose prayers make it all possible.
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"The Spirit and the bride say "Come!" And let him who hears say "Come!" whoever is thirsty, let him come; and whoever wishes, let him take the free gift of the water of life"

(Rev. 22:17)

"Amen, Come Load Jesus"
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"The Effect of Fluid Flow on the Stress Corrosion Cracking of ASTM A508 Cl.2 Steel and AISI Type 304 Stainless Steel in High Temperature Water" CORROSION (to be published)

FIELDS OF STUDY

Corrosion (high temperature corrosion, stress corrosion cracking), Metallurgy (mechanical and Physical)
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1.0 INTRODUCTION

Intergranular stress corrosion cracking (IGSCC) of sensitized Type 304 stainless steel in Boiling Water Reactor (BWR) oxygenated water at high temperature occurs in the heat affected zone (HAZ) adjacent to welds. Accordingly, considerable effort is being made to identify substitute materials that are not prone to stress corrosion cracking (SCC). One of the candidate materials is plain carbon steel.

Indig (1) found that carbon steel is less susceptible to SCC than sensitized Type 304 stainless steel. At 273 °C SCC of carbon steel in air saturated water occurred only in constant extension rate tests (CERT). Transgranular stress corrosion cracking (TGSCC) and pitting of carbon steel SA 333 Gr. (grade) 6 was found to occur in oxygenated water at temperatures in the range of 50-287 °C (2).

The aim of this work is to determine the susceptibility of ASTM A508 Cl. (Class) 2 low alloy carbon steel to pitting and SCC in water containing varying amounts of oxygen at temperatures from 25 to 288 °C. One variable that intuitively could have a large effect upon the susceptibility of alloys to SCC in aggressive environments is fluid flow. Since relative motion between the fluid and the metal surface is known to affect mass transport processes it might also be expected to modify the rate at which a localized corrosion process such as SCC can proceed. However, the author has been able to find very few studies of the effect of flow velocity on the corro-
sion of stainless steels and low alloy steels in aqueous systems at elevated temperatures.

For example, Nesmeyaniva(3) found that, at a flow velocity of 10 m/s, the corrosion rates of stainless steel and low alloy steel in high temperature oxygenated water were decreased by factors of three and 13-16, respectively, compared with the corrosion rates in static systems. To the author's knowledge, flow velocity has not been previously considered as a factor which could influence SCC.

In addition, the effect of strain rate and chloride ion concentration on the SCC susceptibility of ASTM A508 Cl.2 steel was investigated.

This dissertation is divided into four main sections. The literature survey provides the necessary background information. In the section titles "EXPERIMENTAL DETAILS" materials, equipment, and test procedures are described. In the "RESULTS" and "DISCUSSION" sections, the effect of dissolved oxygen, temperature, strain rate, flow velocity, and chloride ion concentration on the SCC behavior of the alloy studied are presented and discussed.
2.0 LITERATURE SURVEY

The term "stress corrosion cracking" is used to denote premature failure by the simultaneous presence of a tensile stress and a specific corrosive medium. The most interesting characteristics associated with SCC are as follows:

- Alloys subject to SCC are passive materials which display corrosion rates less than five mils per year.
- Environmental species which cause SCC are often those which appear innocuous either as regards to identity and quantity.
- SCC can propagate without a specific externally applied stress.
- Only a small fraction of the strength is needed to fracture when exposed to an environment as innocuous as pure water.

Excellent review papers dealing with the SCC of iron-base alloys have been published by Carter and Hyatt(5), Phelps(6), Latanison and Staehle(7), Staehle(8), Theus and Staehle(9), Coriou (10), Berge and Cordovi(11), Nielson(12), Boyd and Berry(13), Sedriks (14), Cheng(15), and Pugh(16). The major factors to determine the susceptibility to SCC are as follows:

- Material: Composition
- Properties: Matrix structure, grain boundaries, strength and toughness
- Influence: Environment (concentration, oxidizer, pH, inhibitor, solvent, temperature), mechanical (mean stress, stress ratio, frequency, wave shape), physical (flow, geometry)

Among the factors the effects of temperature, oxygen, fluid flow, chloride ions, and strain rate will be intensively treated in 3.
this literature survey. In addition, proposed models and the effects of metallurgical factors (alloying elements, cold work, and heat treatment) on SCC behavior will be considered.

2.1 Proposed Models of SCC

The proposed models for SCC can be divided into two groups: those which are approached from the standpoint of dissolution and those which propose that cracking occurs by mechanical fracture. Recently, well-summarized papers were published by Pugh and Bustle (18), Latanison (19), and Latanison and Staehle (7). In the present section the proposed models have been classified according to Pugh and Bustle (18). A schematic of the proposed models for SCC is presented in Figure 1.

2.1.1 Film-Rupture Model

This model was independently originated by Champion (20) and Logan (21) and is sometimes called the slip-dissolution model (22)(23). The basic idea is that a protective film formed in a certain environment is ruptured by localized plastic deformation at the crack tip. The substance is exposed to the environment and rapid dissolution occurs while the remaining substrate is cathodically protected. Figure 2 shows a schematic of this model (22). The crack propagates by the repetition of these steps (repassivation and dissolution by film breakdown). Although this model is simple in concept, its details still remain to be clarified as to whether the crack tip is repassivated completely during crack propagation. Several other investigators agree with the partial repassivation idea (24)(25). On the other hand, Staehle (22)(23) and Vermilyea (26)(27)
Figure 1 Montage showing important processes operating which affect stress corrosion cracking(4)
have proposed that complete repassivation at the crack tip occurs during crack propagation. Pugh and Bustle(18) suggest that the Champion model, modified to include film rupture by slip step emergence, could be a reseasonable model for crack propagation in passivating solutions.

2.1.2 Tunnel Model

Robertson and coworkers(28)(29) first observed tunnel lying primarily on 110 directions in Cu$_3$Au crystals exposed to ferric chloride solutions. Cracks nucleate slip steps by the formation of arrays of fine corrosion tunnels which grow in length and diameter until the remaining metal ligaments fail by ductile fracture as illustrated in Figure 3. Some characteristics of this model are that it applies only to TGSCC, and the fracture surface would be expected to exhibit a series of grooves extending in the direction of crack propagation with the walls between the neighboring grooves matching peak-to-peak on opposing crack surfaces. Dean et al(30) observed this phenomena in Type 304 stainless steel, Type 310 and Inconel 600 after exposure of stressed specimens to boiling MgCl$_2$.

2.1.3 Adsorption Model(Stress Adsorption)

Adsorption of surface active species reduces the fracture stress by reducing the surface energy required to form a crack, as shown in Figure 4. Petch orininally proposed this model(31) and applied to liquid-metal-embrittlement(32), Hydrogen Embrittlement(33), Corrosion Fatigue(34), and SCC(35). This model offers no means of suppressing dislocation generation at the crack tip, and thus it is difficult to explain how a sharp crack could
Figure 2 Schematic representation of crack propagation by the film-rupture model (18)

Figure 3 Schematic of tunnel model (18)
automatically be maintained in ductile materials.

2.1.4 Hydrogen Embrittlement

Several mechanisms have been proposed to explain the effect of hydrogen on the ductility of metals. Louthan and McNitt (36) have succinctly described the various mechanisms listed below:

- The accumulation of molecular hydrogen in internal voids and cracks exerts a pressure which lowers the apparent fracture stress. This pressure model was originally proposed by Zapffe (37).
- A hydrogen-induced decohesion of the lattice proposed by Troiano (38) and modified by Oriani (39).
- Adsorption (stress adsorption) of hydrogen to reduce the surface energy as proposed by Petch (31).
- Beachem (40) suggests that (absorbed) hydrogen-stimulated plastic deformation accelerates subsequent fracture. Though unspecific with regard to the means by which plastically might be affected, recent field ion microscopy by Clum (41) suggests that hydrogen may induce plasticity.
- Formation of a hydrogen-rich phase (e.g. hydride) which has mechanical properties different than those of the matrix (42).
- Hydrogen-dislocation interaction which suppress dislocation glide and provide a means of producing locally large hydrogen accumulation that induces subsequent embrittlement (44) (45).
2.1.5 Selective Dissolution Model (Rupture of a Brittle Film)

In 1959 Forty (46) first described a case of TGSCC of alpha brass in aqueous ammonical solutions where cracks propagated by the repeated formation and rupture of a brittle film growing into the metal at the crack tip. Forty suggested that the selective dissolution of zinc from the alloy results in vacancy injection which, in turn, sufficiently restricts local plastic deformation to permit the initiation of a cleavage crack.

Although this model has not received much attention in recent years, it is still consistent with many of the characteristics of TGSCC, particularly fractography, and it may deserve further consideration.

2.1.6 Tarnish Rupture Model

This model was initiated by Forty and Hunble (47) and developed by McEvily and Bond (48) to explain the SCC of Cu-Zn alloys in aqueous ammonia. Grain boundaries in Cu-Zn alloys are penetrated by the thick tarnish film and, in the unstressed material, this preferential attack attains only a limited depth. In the presence of a stress, the film was observed to undergo repeated rupture as illustrated in Figure 5, thus destroying the transport barrier and permitting continued penetration of the boundaries.
Figure 4 Schematic of adsorption model, which proposes that a specific ion from the environment, X, interacts and reduces the bond strength of a strained bond A-B at the tip of a brittle crack\(^{(16)}\).

Figure 5 Schematic of tarnish-rupture model, modified to incorporate intergranular penetration\(^{(18)}\).
2.2 The Effect of Metallurgical Factors on the SCC Susceptibility of a Material

Among the various metallurgical factors, alloying elements, cold work, and heat treatment are major concerns in this section.

2.2.1 Alloying Elements

Pure metals, with a few exceptions, are believed to be immune to SCC. Many specific instances have been recognized in which small variations in alloying elements produce substantial differences in the susceptibility of SCC. Alloying additions may affect the time-to-failure. Changes in alloy content may also change the failure mode from intergranular to transgranular as occurs when zinc content increases in brass.

2.2.1.1 Nickel

Nickel is a face centered cubic (fcc) metal which is added to stainless steel as an austenitic stabilizer. Nickel does not cause precipitation hardening, but it is believed to influence the distribution of impurities, particularly along the grain boundaries, affecting the ductility of the material. However, some evidences suggest that it can affect the kinetics of precipitation of carbides such as Mo$_2$C, and thus can change both transgranular and intergranular creep strengths. Generally, increasing the solutions by reducing the stacking fault energy of austenitic steels, and thus crack propagation is more difficult. However, in pure water high Ni alloys are more susceptible than intermediate
nickel alloys(55). Staehle et.al(56) proposed a "Nickel Enrichment Model" and postulated that since Ni was more noble, the transient dissolution of the alloy would stop quickly when Ni was added in increasing amounts as an alloying element. Therefore, at low Ni composition, Ni provided the basis for the onset of SCC; however, as the nickel becomes too high, enrichment would occur too rapidly and no dissolution would occur at the slip steps.

2.2.1.2 Chromium

Chromium is a strong compound former. It readily takes part in precipitation hardening reactions with formation of inter-, intra-granular carbides and nitride carbides. The general tendency of the resistance to SCC by the addition of chromium is beneficial but there is a variable effect. Bond and Dundas(56) used U-bend specimen of ferritic stainless steel in boiling 140°C magnesium chloride solution and found that ferritic stainless steel containing 17 to 25% increased the SCC susceptibility of the alloy while additions above and below this range inhibited it. Theus and Staehle (9) and Sedriks(58) have the same opinion on the variable effect of the Cr addition, namely, the effect of chromium on the SCC resistance of an iron-base alloy is dependent on the cracking medium. Staehle et.al.(57) and Osozawa(59) summarized the role of Cr electrochemically: the role of Cr appears to relate to the repassivation kinetics, the general quality of the over-all passivity, and to transient disso-
solution kinetics. The initial addition of Cr to Fe-Ni base alloys reduces the cracking rate due to the results of increasing the kinetics of repassivation. The acceleration of cracking observed as the Cr content of an alloy is increased above 10-15% results from a combination of over-all quality of passivity and of increasing the transient dissolution kinetics.

2.2.1.3 Carbon

Carbon is either in solid solution or present as $M_7C(0,N)$ in the alloy. The effect of carbon on SCC is variable. Staehle (57) and Sedriks (58) have concluded that a beneficial effect results from an accelerated, low intensity and widely distributed pitting action. McIlree et al. (60) found that the L treatment in 316 C was harmful in all environments except in deaerated high purity water. On the other hand, Sandoz (61) showed that carbon in amounts up to about 0.4% (see Figure 6) is detrimental to SCC resistance.

2.2.1.4 Manganese

This element is detrimental to SCC resistance in amounts up to 3% (61). Manganese is an austenite stabilizer and has been used in times of nickel shortage as a substitute for Ni. Adding more than 2% Mn to austenitic stainless steel is detrimental to SCC resistance.

2.2.1.5 Molybdenum

Adding Mo increases the resistance of an alloy to pitting corrosion and also enhance the high temperature mechanical properties of austenitic alloys as well as imparting improved corrosion resistance to alloys when they are exposed to redu-
cing acids. Latanison and Staehele(7) concluded that Mo has a variable effect on the SCC resistance of Fe-Cr-Ni alloys. up to 4% it is detrimental and above this amount it is beneficial. Sandoz(61) found that Mo addition up to 1% had no effect on the $K_{1\text{sc}}$ of the high strength steels.

2.2.1.6 Sulfur

Kowaka and Fujikawa(62) in their study of the effect of S on the SCC resistance of high chromium-nickel alloys concluded that sulfur has a variable effect. Some investigation (57)(63)(64) have found that up to 0.02% sulfur has no effect on the SCC resistance. However, McIIee et.al.(60) stated that high sulfur content in the alloys increased the resistance to intergranular attack in the ferric sulfate-sulfuric acid corrosion test. Wilde and Armijo(65) have found an inhibition effect of sulfur to grain boundary attack, but an increase in general corrosion.

2.2.1.7 Phosphorus

Phosphorus has been shown to be deleterious in magnesium chloride solutions(57)(58). An additional effect is that phosphorous in chloride solutions has been known to accelerate the permeation of hydrogen through the alloys(57).

2.2.1.7 Silicon

Silicon is a well-known film former and accelerates repassivation kinetics(57). A beneficial effect of silicon additions is demonstrated by(6) and (58) in chloride solutions. However, in alkaline solutions(65) and high temperature
chloride solutions(66) alloys containing silicon show cracking. Therefore, it is believed that silicon also has a variable effect. Dreyer(67) found in a study of AISI 4340 SCC susceptibility that silicon which segregates in ε-carbide retards its transformation and its ability to affect the hydrogen evolution reaction and thus improve the resistance of an alloy to SCC

2.2.2 The Effect of Cold-Work on SCC

As long as the constant extension rate test is chosen as the SCC test method to determine the susceptibility to SCC of the alloy, the cold work or pre-strain prior to crack initiation is a very important parameter on the SCC susceptibility since cracks do not nucleate from the onset of straining.

However, limited data are available on the effect of plastic straining for the low alloy steel and stainless steel. Nivak(69) used precracked specimen of HY-180 steel and showed that it remained immune to SCC in artificial sea water following 5% plastic prestrain. Similar tests on HY300 showed that the resistance to SCC was reduced with increasing plastic strain. However, on the presence of cracks or sharp flaws, prestraining(prior to exposure to the corrosive) can have a beneficial effect(70). Therefore, it is believed that cold work is a variable which can interact with the metallurgical state of the material and produce effects on the SCC not readily interpretable in terms of gross strain. Obtaining more data on stainless steel can give a clearer picture about this effect of cold work.
Earlier work by Bain et al. (71) showed that cold work prior to sensitization of austenitic stainless steel greatly reduce the susceptibility zone on the time-temperature diagram. Tedmon et al. (72) demonstrated that 55% cold work eliminated grain boundary or general attack in the boiling Strauss solution (acid copper solution). Recently, Briant et al. (73), in the study of the effect of pulling Type 304 stainless steel specimen in tension to stresses of 345 to 552 MPa, found that whereas prior cold work hastened the onset of sensitization, a larger cold work resulted in complete healing. Although the annealed Type 304 stainless steel is not prone to cracking intergranularly in oxygenated high temperature water, TGSCC occurs in pure water containing 0.2 and 200 ppm of oxygen at 288°C if the material is cold worked above 30%.

One interesting aspect observed by Clarke and Gordon (74) is that a substantial decrease in time-to-failure was observed in the range of 20 to 30% of cold work. Picket and Sim (75) also found an increased susceptibility to SCC for 304 stainless steel cold-worked 5 to 20% prior to sensitization. Recently, Pedneker and Sialowska (76) found the same results using the CERT technique in sulfuric acids at room temperature; less than 5% cold work can result in extreme SCC susceptibility but high amounts of cold work (50-60) causes a complete healing of sensitization. Cowan and Gordon (77) explained the effect of cold work on the increase in SCC susceptibility by these two combined effects: first, the cold working induces an increase of yield strength and allows the application of a high-
er load, especially with fixed deflection samples. Secondly, the cold working produces deformation-induced martensite as observed by Vermilyea and Indig(78).

Pedneker and Smialowska(76) concluded that the increased susceptibility induced by the small amount of cold work is due to a faster nucleation and/or growth of chromium carbides, and therefore, more severe chromium depletion occurs near the carbides. In the highly cold worked case there is no continuous chromium-depleted region.

2.2.3 The Effect of Heat Treatment and Microstructure on SCC Susceptibility

Various heat treatment are known to relieve residual stress, homonize structure, cause precipitation of stable phase, increase grain size. Whatever the heat treatment are, all the functions performed by the heat treatment have relevance to stress corrosion cracking. For example, stress relief heat treatment reduced SCC of brass as observed by Rosenthal and Mazia(79). In the case of Type 304 stainless steel, it is well-known that intergranular SCC occur by heating a specimen into the sensitizing region for a sufficient period of time. For convenience, sensitization of Type 304 stainless steel is not treated in this section but many investigations have reported excellent works(68). As another example of the effect of heat treatment on the susceptibility of alloys to SCC, cracking susceptibility in forged aluminum bronze alloy has been reduced by homogenizing the structure(80).

In this section, the particular effects of quenching and
and tempering on the SCC susceptibility are considered in detail. The second half of this section will review the causes and characteristics of stress relief cracking (i.e. intergranular cracking in the heat affected zone) that occurs during the exposure of welded assemblies at the temperatures produced by postweld heat treatments or high temperature services.

2.2.3.1 The Effect of Quenching and Tempering on SCC Behavior

The trend of increasing tempering temperatures and times is favorable to increase SCC resistance (81-83) as illustrated in Figure 7 and 8. Tiner and Giplin (82) studied the effect of tempering temperature on SCC resistance for 4340 steel in a 3% NaCl solution saturated with oxygen and acidified to a pH of 1.5; a 300 F tempered condition there was no failure in 100 hours. It was found that there are sometimes intermediate temperatures which produce a maximum susceptibility in the material (see Figure 7).

It has been suggested that the beneficial effect of increasing tempering temperature results from less \( \phi \)-carbide and more cementite in the microstructure (82), but this suggestion has not been generally supported (84). In addition, the distribution of carbides is also an important factor (85)(86). A uniform distribution of spheroidal carbide is the best condition for the beneficial effect of heat treatment on the SCC susceptibility. Benjamin and Steigerwald (86) in a study of the detrimental effect of untempered material on SCC susceptibility
suggested that martensite plate boundaries and transformation twins are known to be favorable nucleation sites for carbide precipitation, and hence, may also provide preferential and easy paths for crack propagation.

The importance of χ-carbide in the SCC process was briefly described by Tiner and Giplin(82) as follows:

- Cathodic microregions were present when specimens were tempered in a temperature range where χ-carbide exists, but were absent when χ-carbide completely transformed to cementite.

- χ-carbide powder, by reaction of Fe with C, has the characteristics of absorbing H in quantities up to 1.4% wt. (84)

- TEM studies showed that chemical attack takes place in regions immediately surrounding χ-carbide precipitates.

- Stress corrosion cracking paths appears to be associated with the microregions where χ-carbides tend to precipitate, namely, austenite grain boundaries and (100) martensitic planes (flat semi-cleavage regions on the fracture surface) (85). Therefore, they concluded that the SCC resistance of AISI 4340 may be improved by minor changes in one of the alloying elements (86)(87). They also found that polarization curves of the tempered martensite low alloy steel specimens appeared to shift in the electropositive direction with increasing tempering temperature.

Recently, Parkins(87) demonstrated that the apparent disagreement in the literature between the results of various workers who have studied the effect of quenching and tempering
Figure 6 The Effect of carbon on the stress corrosion cracking of AISI 4340 steel quenched and tempered to either 172 or 192 ksi yield strength(61)

Figure 7 Effect upon the time-to-failure ratio of variables quenched steel tempered for 1 h at different temperature(81)

Figure 8 Effect of different tempering times upon the time-to-failure ratio of 2 steels tempered at various temperatures(82)
upon the SCC of carbon steels in a nitride environment, is due to their use of steels of different carbon contents. He found some interesting points:

- Higher carbon steels (0.1%) are more susceptible to cracking than lower carbon steels, in the quenched condition.
- In the CERT, the higher C steels show an increase in susceptibility to cracking after tempering at low temperature. In contrast, low carbon (0.05%) steels show an increase in susceptibility upon tempering at high temperature.
- Prolonged tempering time moves the maximum resistance to cracking to lower temperatures.

Regardless of carbon contents, a sufficiently high tempering temperature and prolonged tempering time promote recrystallization and increase cracking susceptibility.

The effects of the carbon content and structure may be partly due to their effect upon the mechanical and macroscopic electrochemical properties.

It appears probable that tempering influence the electrochemistry of cracking through its effect upon the microscopic distribution of attack sites rather than any macroscopic effect reflected in polarization.

2.2.3.1. Stress Relief Cracking of ASTM A508 Cl.2 Steel

A508 steel exhibits good weldability and formability. Experience has shown that when welded with high input energy processes such as submerged-arc and electroslag welding,
the base metal adjacent to the fusion boundaries is prone to stress relief cracking during post weld heat treatment at 600 °C (88-93). A typical heat treatment involves austenizing at 860°C-910°C for 4-8 hours followed by quenching and tempering at 650 - 690°C. The exact temperature depends upon the precise chemical composition. After welding (cladding) post weld heat treatment between 550 to 620°C is conducted for a cumulative time of 40 hours.

Figure 9 illustrates the location and orientation of underclad cracks (stress relief cracks) relative to the maximum temperatures reached by the heat-affected zone. According to the investigators (94-96), surface preparation is one of the variables to affect the susceptibility to cracking; a machined surface is more susceptible to cracking than is the steel in the as-rolled and shot blasted condition.

One generally accepted cracking mechanism is that cracking occurs during post weld heat treatment (PWHT) when the creep ductility of the heat affected zone (HAZ) (or weld metal) is not sufficient to absorb the plastic strain occurring as a result of relaxation of residual stresses introduced by the welding operation (97, 98). Dolby and Sanders (93) summarized the principal factors (composition, microstructure, and residual stress) which affect the mechanism of cracking.

- Alloying elements can affect cracking susceptibility in two ways (a) by affecting transgranular creep strength and (b) by affecting grain boundary ductility. An attempt was made by Nikiet et. al. (99) to quantify susceptibility in terms of
major alloying additions as follows:

\[ G = Cr + 3.3Mo + 8.1V - 2 \]

where, \( G > 0 \) susceptible, \( G < 0 \) not susceptible

- a major feature of microstructure is the prior austenite grain size of the HAZ and also the extent of the grain coarsened region. Data(100-102) show that coarse austenite grain sizes are more susceptible to cracking.

- Residual welding stresses and the strains occurring during their relaxation at elevated temperatures are major factors in cracking.

From these mechanistic understandings, prevention techniques are developed and applied to the field but still there is room for improvement:

- control alloying elements; low C content is beneficial
  - grain refinement practice
  - reduce residual stress and impurity level

- changes in cladding procedures; low energy input,
  - double energy technique
  - renormalizing technique

- change in PWHT procedures; reduce PWHT temperature to less than 600 C, a controversial modification of this treatment(103) would be to try a two stage PWHT with a 2 hrs at 500 C treatment before heating to 610 C(104)
2.3 Environmental Influence on SCC Susceptibility

Among the structural steels of the nuclear reactor vessel Type 304 s.s. has been studied by numerous investigators during the last decade(105). Carbon steel and low alloy steel have not attracted much attention for study in BWR environment, and there are little data available for the environmental effects on the SCC susceptibility for these materials. In this section, data are presented and analyzed for iron-base alloys. The environmental fluid flow, chloride ion concentration, and strain rate. As mentioned in the introduction the transient period of startup and shutdown operations of a power plant drastically effects the first two factors (temperature and oxygen). Intuitively, flow rate could also have a large effect upon the susceptibility of alloys to SCC in aggressive environments. Each of these factors are related to the formation of corrosion products, corrosion rate, and potential

2.3.1. The Effect of Temperature on SCC Susceptibility

In order to determine the susceptibility of a material to SCC there are several methods of data analysis such as time-to-failure, crack propagation rate, etc.. The literature, by using these parameters to determine SCC susceptibility, demonstrates that the experimental results are divided into two groups. The first group is that in which crack propagation rates exhibit linear dependency upon temperature. The other group is that in which crack propagation rates are maximized at a certain temperature.
In Figure 10, Hoar\cite{106} indicates that an increase in temperature from 125 to 154°C causes a considerable decrease in the time-to-failure of 304 s.s. in MgCl$_2$ solution. In Figure 11, White\cite{107} recently obtained results of the temperature effect on SCC, which demonstrates a straight relationship. Flis\cite{108}, in the study of SCC behavior of Armco iron in 5M NH$_4$NO$_3$ at 25-100°C, showed that the characteristics of an oxide film are responsible for SCC; the high rate at high temperature under open circuit conditions was ascribed primarily to the rapid formation of the repassivating $\alpha$-Fe$_2$O$_3$ film. The same linear dependency was observed in high strength steel\cite{109,110}.

On the contrary, Frey and Staehle\cite{111} observed, in a study of SCC behavior of Fe-Ni-Cr alloy in a chloride solution, that time-to-failure was minimum at 177°C as presented in Figure 12. They suggested that the oxide build-up rate (or at least oxide integrity) at 177°C is very much lower than at the higher temperatures, and slip step emergence is relatively easy over a long period. They concluded that the effect of relative resistance to slip step emergence appears to be more significant than the possibly increased dissolution at higher temperatures. The discovery of SCC in the sensitized s.s. cladding of a Japanese BWR led Kondo to initiate the first experimental program on the effect of a simulated water cooled reactor environment on fatigue crack growth for ASTM A508 steel\cite{112}. They showed that the crack acceleration was dependent upon the test frequency and water temperature, as shown in Fig.
Figure 9 Location and orientation of underclad in relation to the maximum temperatures reached by HAZ

Figure 10 Variation of time-to-failure with temperature (304ss.)
Figure 11 Temperature versus true strength at various dissolved oxygen concentration (107).
Figure 12 Corrosion and SCC behavior of A302 B steel

Figure 13 Effect of temperature on crack growth in deionized water of A302 B steel
13. They also found a similar behavior of corrosion rate with temperature in Figure 12. They explained this behavior in two ways: (a) the kinetics of the early stage corrosion and (b) the formation of micro-fissures at the crack tip. They hypothesized that:

- the increasing stability of the protective magnetite oxide with increasing temperature may influence the corrosion rate toward the direction of protecting the metal from corrosion,
- the formation of microscopic corrosion pits within the cracks in the environment typical for a BWR temperature may blunt the crack tip and retard the advance of SCC(114).

Recently, Ford and Povich(115) explained the effect of temperature on SCC susceptibility in terms of the interrelationship between the open circuit potential, temperature, and crack propagation in their study of sensitized 304 s.s. to SCC susceptibility in high purity water as shown in Figures 14 and 15. A decrease in temperature would be expected on an activation enthalpy basis to give a decrease in crack propagation rate, but under open circuit potential conditions, for a given oxygen concentration, this temperature decrease will anodically polarize the specimen (see Figure 15), thereby leading to a possible increase in crack propagation rate; the net effect will depend upon the relative driving force of these two rate controlling parameters (potential and temperature) in a given potential range. Thus, with respect to the result in Figure 14, the increase in crack propagation rate in changing from 288°C to 200°C is due to the fact that the specimen is being
anodically polarized in a potential region where the rate determining step in propagation has a low activation enthalphy, whereas a further decrease in temperature to 100°C gives rise to a decrease in crack propagation rate since the potential has been moved into a potential regime where the rate determining step in propagation has a high activation enthalphy for the straining condition used in the test.

The same results have been compiled by Ford (118) for stainless steel and low alloy ferritic steels in low oxygen solution. Pao and Wei (119) made interesting comments on this phenomena: the complex shape of the curve of crack propagation rate vs temperature is indicative of multiple controlling mechanisms being active at low temperatures, and a difference in slope is indicative only of different rate controlling processes, and not necessarily of a different embrittlement mechanism.

2.3.1.1. The Effect of Temperature on Polarization Curve

Only a few anodic polarization curves have been obtained for 304 s.s. and mild steel in the range of 100 and 200°C. They are by Lee (120) in Figure 16 and by Fujii (121) in Figure 17. With increasing temperature the corrosion potential and the potential of the transpassive peak decreases, while the passive current increases for quenched and sensitized 304 s.s. in 0.1N Na$_2$SO$_4$. Figure 15 shows the potentiodynamic polarization curves for mild steel in the same solution. Active dissolution is observed below 150°C in the anodic curves. A passive region appears at 200°C. Although polarization yield valuable
Material: Quench Annealed Type 304 S.S.
Solution: 0.1N Sodium Sulfate
Scan Rate: ~20 Minutes at Each Potential

Figure 16 Effect of temperature on anodic polarization curves of Type 304 stainless steel in deaerated 0.01 N Na₂SO₄ solution(120)
information about the anodic behavior of metals, except for pitting, no other type of localized corrosion behavior can be predicted from the curve itself.

2.3.1.2 The Effect of Temperature on the Corrosion Rate

Fraunhofer (122) demonstrated the effect of temperature on corrosion rate as a function of the nature of systems in Figure 18. In a closed one, the corrosion rate doubles for every 30°C in temperature until all the oxygen is consumed; the rate then falls to a very low level. However, in open system the corrosion rate is increased linearly with temperature until the fall in solubility of oxygen outweighs the acceleration effect of temperature, and then it falls.

A similar behavior has been observed by others (123, 4). The corrosion rate is max. at 93 to 123°C for Type 304 stainless steel. Researchers suggest the controlling mechanism is as follows: the peak is due to the competition between (a) increased oxide formation by creating metal ions and (b) retarded oxide formation by the formation of protective oxide that hinders the conversion of metal into ions. However, over the wide range of temperatures and oxygen contents the results are not consistent. A recent study by Mizuno (123) of the effect of temperature and oxygen on the corrosion rates for SA106Gr.B and 333Gr.6 carbon steels in high purity water shows that the corrosion rate is a function of dissolved oxygen and temperature as shown in Figure 19. They found a maximum corrosion rate at 175°C in water containing 8 ppm (2.5x10⁻⁴ M) oxygen.
Figure 17  Potentiodynamic polarization curves for mild steel in deaerated 0.1 N Na$_2$SO$_4$ solution (scan rate 50mV/min) (121)

Figure 18 Variation of corrosion of iron with water temperature, open and closed systems (schematic) (122)
Figure 1.9 Effect of temperature on the corrosion loss of SA 106 Gr.B and SA 333 Gr.6. Exposure time: 200 hrs; Arrows: 95% certification limit (123)
a minimum value at 175°C to 250°C in 1 ppm of oxygen. In low oxygen water (0.015 ppm) the corrosion rate is increased with temperature above 100°C. Therefore, it is believed that the corrosion rate is a function of temperature, oxygen, nature of system, and possibly flow velocity.

2.3.1.3 The Effect of Temperature on Corrosion Products

Bloom (124) states the eight products known to form during corrosion of steel in aqueous environment as shown in Table 1. Above 122°F (50°C) to 1058°F (570°C) in deaerated water magnetite is a stable oxide, and in oxygenated water hematite is formed. Below 50°C in deaerated water Fe(OH)₂ and Fe₃O₄ are present. In oxygenated water near R.T. the corrosion product formed on iron is non-adherent ϕ-FeOOH. The ϕ-FeOOH is transformed to non-adherent ϕ-Fe₂O₃ by raising the temperature of the system to above 315°C. For 304 s.s., the effect of temperature on corrosion products was thoroughly investigated by Castle and Clayton (125, 126). They found that the film growth kinetics are different in different temperature ranges; at 200°C the film thickness increased almost linearly with time, but at temperatures ranging from 40 to 60°C a logarithmic rate law was obeyed. This fact is indicative of the different mechanism of SCC taking place at high and low temperatures.

2.3.2 The Effect of Dissolved Oxygen on SCC Susceptibility

During the last decade the effect of oxygen on SCC suscep-
Table 1 Corrosion products of iron(II)4

<table>
<thead>
<tr>
<th>Composition (Mineral name)</th>
<th>Color</th>
<th>Structural type</th>
<th>Magnetic character</th>
<th>Electrical Resistivity</th>
<th>Density</th>
<th>Thermal behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃O₄ to Fe₇O₈ (Wustite)</td>
<td>Black</td>
<td>NaCl</td>
<td>Paramagnetic</td>
<td>Semiconductor</td>
<td>5.4-5.73</td>
<td>Melts at 1371°-1424°C. Below 570°C decomposes to Fe and Fe₂O₃.</td>
</tr>
<tr>
<td>Fe(OH)₃ (Peroxide)</td>
<td>White</td>
<td>Mg(OH)₂ (Brucite)</td>
<td>Paramagnetic Insulator</td>
<td></td>
<td>3.40</td>
<td>Decomposes at about 100°C to FeO and H₂O.</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>Black</td>
<td>Spinel</td>
<td>Ferromagnetic Electronic conductor</td>
<td>5.20</td>
<td></td>
<td>Melts at 1597°C</td>
</tr>
<tr>
<td>γ-FeOOH (Lepidocrocite)</td>
<td>Orange</td>
<td>γ-FeOOH (Lepidocrocite)</td>
<td>Paramagnetic Insulator</td>
<td></td>
<td>3.97</td>
<td>Dehydrates to γ-Fe₂O₃ at about 200°C</td>
</tr>
<tr>
<td>α-FeOOH (Goethite)</td>
<td>Yellow</td>
<td>α-FeOOH (Goethite)</td>
<td>Paramagnetic Insulator</td>
<td></td>
<td>4.20</td>
<td>Dehydrates to α-Fe₂O₃ at about 200°C</td>
</tr>
<tr>
<td>γ-Fe₂O₃ (Maghemite)</td>
<td>Brown</td>
<td>γ-Fe₂O₃ (with vacancies)</td>
<td>Ferromagnetic Semiconductor</td>
<td></td>
<td>4.88</td>
<td>Transforms to γ-Fe₂O₃ above 250°C</td>
</tr>
<tr>
<td>α-Fe₂O₃ (Hematite)</td>
<td>Brick red</td>
<td>Al₂O₃ (Corundum)</td>
<td>Paramagnetic Insulator</td>
<td></td>
<td>5.25</td>
<td>Decomposes to maghemite at 1457°C and 1 atm</td>
</tr>
</tbody>
</table>

* Color indicates that these are insulators.
† In contact with traces of oxygen Fe(OH)₃ is unstable at room temperature and transforms to γ-FeOOH, α-FeOOH, or Fe₂O₃ depending on the conditions of the system.
‡ Presence of water causes conversion to α-Fe₂O₃ at lower temperatures.
tibility of sensitized Type 304 stainless steel was intensively investigated by many researchers in BWR-type water\((68, 107, 115, 127-132)\). Recently, Ford\((118)\) has conducted constant extension rate tests for carbon steel to examine the combined effect of temperature and oxygen concentration. Based on these literature, SCC susceptibility of iron-base alloys will be reviewed.

Generally, in SCC testing, two test methods are used, the CERT and constant load test. The results of these two different approaches reach the same conclusions except for a few discrepancies. In constant load tests conducted at oxygen concentrations ranging from 0.2 to 5 ppm, the time-to-failure decreased with increasing oxygen concentration\((132)(130)\). In an early work by White et.al.\((132)\) the effects of oxygen concentration at 288 C on the cracking susceptibility of Type 304 stainless steel at the different sensitizing times are shown in Figure 18. In Figure 19, Clarke and Gordon\((130)\) found similar results of the oxygen effects at the different stress levels. They observed an increase in failure time for the constant load specimen tested above 100 ppm of oxygen regardless of stress level. They postulated that oxygen induced acceleration in cracking between 0.2 and 3-5 ppm of oxygen might be due to one of the following facts:

- the supply of oxygen to the specimen surface may be diffusion limited
- the increase in electrochemical potential from dissolved oxygen may oxidize the Cr containing film to the Cr\(^+\) state
Figure 20 Effect of oxygenated water on SCC susceptibility (132)
Figure 21 Effect of oxygen concentration on the IGSCC of sensitized Type 304 stainless steel (from one heat) in 288 °C water at two applied stress levels.
the electrochemical driving force controlled by the difference between the bulk surface potential and the potential at the oxygen depleted crack tip.

The small initial drop in pH caused by larger additions may accelerate anodic dissolution during the initiation phase.

In CERT(68,115,118,125,131) the average crack propagation rate was used as a parameter to determine the SCC susceptibility. The general trend of crack propagation rate is similar to the results of constant load tests, namely, crack propagation rate increases with an increase in oxygen concentration from 0.1(3.1x10⁻⁶M) to 32 ppm(10⁻³M)(see Figure 22).

Welch(68) found IGSCC of Type 304 stainless steel in high purity water containing oxygen from 0.8(2.4x10⁻⁵M) to 32 ppm (10⁻³M) at 200 C and at 250 C IGSCC occurs above 0.1 ppm(31x10⁻⁶M) of oxygen. Below 0.1 ppm(3.1x10⁻⁷) oxygen at 250 C and 200 C he observed TGSCC as shown in Figure 20. He explained the effect of dissolved oxygen as follows: the role of oxygen in the IGSCC process is to increase the corrosion potential into the transpassive region where the current density is high enough for significant dissolution of materials to occur following a film rupture event. For TGSCC, the oxygen does not affect the corrosion kinetics, and the crack propagation rate is independent of oxygen concentration.

It is interesting to compare the results of the different testing methods. White (132) did not observe IGSCC in pure water containing 1 ppm(3.1x10⁻⁶M) and 4 ppm(1.2x10⁻⁵M) O₂. 
Figure 22  Estimated crack propagation rates of sensitized Type 304 stainless steel in high temperature water as a function of dissolved oxygen concentration(68)
contrary to Welch’s result. IGSCC was observed by Welch but not by White in water containing 8ppm of oxygen at 121°C. Ford and Povich (115) using CERT reported IGSCC at 50°C in the presence of 1 and 8ppm of oxygen and also at 100 and 150°C. As mentioned in the previous paragraph, Welch found TGSCC below 0.1ppm oxygen, but no SCC was found to occur. In Figure 23, Cragnolino and Smialowska (133) summarized the combined effects of oxygen content and temperature at which IGSCC and TGSCC have been found to occur in CERT.

To the author’s knowledge, there is only one paper available which shows the effect of oxygen on the SCC susceptibility of carbon steel (see Ford (110)). Ford’s results are illustrated in Figure 24. The cracking mode of SA 333 Gr. 6 carbon steel in CERT is purely TGSCC. TGSCC and Pitting are observed in BWR water.

2.3.2.1 The Effect of Oxygen on Corrosion Rate

Since 30% of the U.S. Navy boiler tube failure reported in 9152 (134) were caused by corrosion from oxygen (> 100 ppb), several researchers have studied the effect of oxygen on the corrosion behavior of carbon steel (135-137). They found that, in the presence of high oxygen (> 100ppm), carbon steel was well protected from pitting and general corrosion, but that there are intermediate oxygen levels which promote pitting. Ruther and Hart (113) studied the corrosion of pure iron in distilled water over a range of temperature (50-315°C) and oxygen content (0.1-540ppm). Their work showed that a uniform
Figure 23 Stress corrosion cracking susceptibility of sensitized Type 304 stainless steel in pure water for different oxygen concentration/temperature (133)
Figure 24: Variation of pitting and crack depths with oxygen-temperature combination (110)
brown-black coating of magnetite formed in low oxygen water (\( < 0.1 \text{ ppm} \)) at 315 \( \text{C} \). Severe pitting developed in water containing an intermediate concentration of oxygen (35 ppm, 1.1 \( \times 10^{-3} \text{M} \)) over the entire temperature range from 52 \( \text{C} \) to 315 \( \text{C} \). Cheng(139) pointed out that dissolved oxygen in sufficient quantity might be desirable for carbon steel, but that it would release a high concentration of chromate in the cases of austenitic stainless steel and Inconel. Dissolved oxygen generally has little effect on the steady state corrosion rates of austenitic stainless steel and Inconel, but the solubility of the corrosion products must be affected substantially, and therefore, oxygen affects the release of these products. Uhlig(139) illustrated similar data in Figure 23, namely, an increase in the dissolved oxygen level results in a near linear increase in corrosion rate to a maximum.

Videm and Aas(123) found that corrosion in the water phase of a static system (1) is inhibited by 0.1 to 10 ppm of oxygen, (2) is increased by 10 to 100 ppm of oxygen, and (3) is again inhibited above 100 to 800 ppm of oxygen.

Recently, Brush and Pearl(123) reported that oxygen is an effective inhibitor in neutral pH feedwater, preventing significant corrosion product generation and release in concentrations as little as 15 ppb (5 \( \times 10^{-7} \text{M} \)) to 30 ppb (10^{-6}), and is still effective with 2 ppm (6.2 \( \times 10^{-5} \text{M} \)). The presence of oxygen drastically reduces the bulk stream ferrous ion concentration by making the ferric ion the stable ion(124), so that the oxidation process is controlled by diffusion in liquid micropores(141).
In Figures 24(142) and 25(143) data are presented for the effect of oxygen on the corrosion rates of carbon steel and alloy steel. Heitz(143) et.al. observed that, regardless of alloy composition, the corrosion rate is a maximum at an oxygen concentration of 10 ppb (3.1x10^{-7} M). They superposed the corrosion reaction of the oxygen electrode on the hydrogen electrode as shown in Figure 26, and concluded that, at the lower oxygen concentration (10 ppb: 3.1x10^{-7} M), hydrogen evolution was a predominant cathodic reaction.

2.3.2.2 The Effect of Dissolved Oxygen on Corrosion Products

In this part, corrosion products formed on iron and iron-base alloys in high temperature aqueous environments (deoxygenated and oxygenated) are considered.

Corrosion products in oxygenated water

The oxide formed during startup of BWR, before adding oxygen, is in the form of a double layer of magnetite (Fe$_3$O$_4$), as observed by Potter and Mann(144). The formation and growth of this double magnetite layer has been widely studied(145-162). Recently, Mann published an excellent review paper(146) on this subject. The structure and development of the double layer is illustrated in Figure 27. The inner layer grows at the metal/oxide interface. The inner layer frequently occupies the same volume as the metal which has been oxidized(150, 151, 154) and it is not dissolved at its outer surface(151). In many solutions the inner layer has
Figure 25 Variation of corrosion of iron with dissolved oxygen content (schematic) (139)

Figure 26 Corrosion rates from weight vs. oxygen content: ○ steel C15, Δ Base metal, + Base melt + 5.5% Ni, × Base melt + 6.0% Cr (142)
Figure 27: Corrosion of carbon steels vs. oxygen (143)
Figure 28: Superposition of corrosion by oxygen and acid (i.e. water) produces a minimum of total corrosion (143)

Figure 29: Schematic development of double magnetite layers. 1. nuclei at metal surface. 2. initial growth of oxide crystals. 3a. growth of inner layer beneath the crystals. 3b. protective outer crystalline layer. 4a. fully developed double layer. 4b. breakdown of outer layer with formation of inner layer pits (146)
been shown to be porous by density measurement(151), by gas adsorption(154), and by microscopy(152-154), although there may be a thin-porous layer at the metal/oxide interface(155, 163,164). The size and form of crystals in the outer layer are strongly influenced by the solubility and concentration of iron in the environment(controlling growth)(155), and by the surface preparation(controlling nucleation)(147)(152). It is generally accepted that, in both high and low pH solutions, the outer crystalline layer is formed by precipitation of iron ions, which have dissolved at the metal surface and diffused in the solution through the pores in the inner layer. The porous inner layer may be generated by partial dissolution or by recrystallization of a barrier layer at the metal surface. A similar growth mechanism probably operates in pure water, through other mechanisms of ionic transport may become important at low rates of corrosion.

Corrosion products in oxygenated water

According to the Pourbaix diagram, in Figure 28, there are two thermodynamically stable oxides in neutral solutions at elevated temperatures—magnetite and hematite(167). Many workers(123,165-170) report these oxides to form on steel in water containing oxygen. The addition of oxygen to the solution causes the outer layer to be oxidized to \(\gamma\)-Fe\(_2\)O\(_3\). Magnetite is formed next to the metal and is overlaid with hematite. At high concentrations of oxygen(\(>130\text{ppm}, 4\times 10^{-3}\)M), well-crystallized films of hematite only have been found(138).

These uniform films result in a decrease in corrosion.
Figure 30 Potential-pH diagram for $\text{H}_2\text{O}$-Fe at 250 C and 350 C (167)

Figure 31 Schematic representation of oxide formed on carbon steel exposed in representative BWR environment(138)
a decrease in corrosion rate in high oxygen concentrations. Magnetite is easily oxidized in aqueous environments to $\gamma$-$\text{Fe}_2\text{O}_3$ (magnetite) without alteration of the structural framework (166). Mann (146) speculated that this reaction possibly can be the mechanism of formation of the hematite in the presence of oxygen. He also suggested that pitting attack is due to this localized transformation of the protective spinel ($\gamma$-$\text{Fe}_2\text{O}_3$) to non-protective $\gamma$-$\text{Fe}_2\text{O}_3$.

2.3.2.3 The Effect of Dissolved Oxygen on the Potential

There are much data available (117, 120, 123) for Type 304 stainless steel and carbon steel on the effect of dissolved oxygen on the corrosion potential in the high purity water. The results are presented in Figures 30-33. The first two figures are for sensitized 304 s.s., and the last two are for carbon steel. Although the results are different in details the general trend is the same regardless of materials and researchers. They found that for a given oxygen content an increase in temperature results in a decrease in corrosion potential, and for a given temperature an increase in oxygen results in increasing corrosion potential. Also, they report that the corrosion potential at low oxygen contents is controlled by the hydrogen ion reduction, while in the high contents the potential is controlled by oxygen reduction. Indig (1) reported that the potential increases most rapidly in the 0 to 0.05 ppm ($1.6 \times 10^{-7}$M) range of oxygen. In the range of 0.05 ppm ($1.6 \times 10^{-7}$M) to 8 ppm ($2.5 \times 10^{-4}$M) of oxygen the po-
Figure 32 Corrosion Potential of Type 304 stainless steel as a function of dissolved oxygen concentration in high purity water at various temperatures.
Figure 33 The effect of dissolved oxygen concentration on the corrosion potential of Type 304 stainless steel in high purity water at 274°C (123)
Figure 34 Potential/Oxygen summary (118)
Figure 35 Effect of oxygen concentration on Corrosion Potential of SA106Gr.B steel (123)
tential changes are less pronounced. Thus, if the corrosion potential is the major environmental factor in the SCC of carbon steel, it would be expected that significant mitigation of SCC would occur below the 0.05 ppm (1.5x10^{-7} M) of oxygen level.

2.3.3. Effetc of Fluid Flow on Corrosion Behavior

Fluid flow is known to be one of the parameters to determine SCC susceptibility of materials in aqueous environments. One or both of the initiation and propagation processes of cracking could be influenced by flow rate. In this section on corrosion rate and corrosion products will be considered.

2.2.2.1 General Effect of Flow Velocity

Uniform environments can be attained by a slight motion of fluid (Re < 2100) and localized corrosion is prevented. Generally, increasing flow velocity increases corrosion by supplying the corrosive at a faster rate, but it may also decrease corrosion by replenishing inhibitors of corrosion, particularly at crevices and other stagnant places. In the turbulent regime the flow produces non-uniform conditions and pitting is likely to occur. When the flow velocity becomes high, mechanical effects add to the damage of metal. In these high velocity flow regime, so-called erosion-corrosion becomes dominant in the corrosion processes. Therefore, the effects of flow velocity on the corrosion behavior of iron-base alloys and carbon steels are varied.
and carbon steels are varied.

2.3.3.2 Flow Effects on Corrosion Rates

Many papers have been published on the effect of flow rate on the corrosion rate of iron and iron-base alloys in aqueous environment. Corrosion rate in a flowing solution is a function of oxygen concentration, temperature, velocity, and solution pH (173-185).

The corrosion rates in flowing solutions differ depending upon the oxygen concentration in the solution. Brush and Pearl (185) demonstrated that in neutral pH feedwater containing 200 ppb($6.2\times10^{-7}$ M) of oxygen and 25 ppb($2.5\times10^{-8}$ M) of hydrogen, the release behavior of carbon steel is not affected significantly by velocity, but in water containing 3 ppb($9.3\times10^{-9}$ M) oxygen the effect of velocity is more pronounced. Ross et al. (176) in their studies of the anodic behavior of iron-carbon steel in moving media (acid) reported the opposite results. Namely, in an oxygenated solution, the shifting of the rest potential and polarization curve in the positive direction is more pronounced on increasing the flow velocity. But, in a deaerated solution, the rest potential is insensitive to flow velocity due to the fact that the reactions involves are entirely activation controlled. The same results were reported by Foroulis and Uhlig (175) for carbon steel in sulfuric acid as illustrated in Figure 34. This is indicative of the fact that the solution pH is another variable which affects the corrosion rate in flowing solutions (see Figure 35).
Increasing temperature may cause little change\( (177,178) \), a decrease\( (179) \) or an increase\( (180,181) \) in the corrosion rate of copper alloys in flowing aerated water. At 34°C a linear dependency of fluid flow velocity on corrosion rate was found by Brush and Pearl\( (185) \). Similar results were reported by other investigators\( (147,183) \). However, at 204°C Brush and Pearl\( (185) \) found that the rate increased as the velocity increased from 6 to 12 fps\( (1.8 \text{ to } 3.6 \text{ m/s}) \), and an inversion in corrosion rate at 24 fps\( (7.2 \text{ m/s}) \) was reported to result from the formation of protective oxide film. Nesmeyanova\( (3) \) et.al. reported in a study of the effect of oxygen on the corrosion rate of low alloy steel in 300°C water containing 8 ppm\( (2.5 \times 10^{-4} \text{M}) \) of oxygen, Figure 36, a decrease in the corrosion rate of low alloy steel with an increase in the flow rate.

2.3.3.3 Flow Effect on the Formation of Oxide Film

Flow velocity has an effect on the conditions under which oxide films are formed, and thus, it can affect the protective character of the oxide films. In low flow velocity water containing oxygen, ferric hydroxide might be precipitated on the metal surface and be protective. Whereas, at high velocities, ferrous products might be precipitated away from the metal surface and be non-protective\( (173) \)

Butler and Stout\( (184) \) found similar results on the influence of movement and temperature on the corrosion behavior of mild steel. The amount of geothite, \( \alpha -\text{FeOOH} \), in the corrosion product increased with flow velocity, and was indicative of a higher rate of oxidation.
Figure 36 Effect of velocity on corrosion rate of carbon steel (174)

Figure 37 Variation of corrosion of iron with pH at high flow rates (174)

Figure 38 Effect of water velocity on corrosion losses of low alloy steel No. 4 at 300 C oxygen content: 7-10mg/l

1. 300-hr test
2. 1050-hr test
of the ferrous ions initially formed. The decrease in corrosion rate at the highest floe velocity studied is attributed to the formation of a more protective oxide film.

Thus far, the corrosion behavior at low temperature has been considered. At elevated temperatures, in flowing pure water systems, precipitation of the outer layer of the magnetite double layer is completely inhibited\(^{(186)}\), probably because the concentration of iron in the pure water streams is held below the solubility of magnetite\(^{(145)}\). The protective oxide film present on iron in flowing water can be improved by the addition of alloying elements. For example, chromium and aluminum in elemental form are well-known for their tenacious and protective films.

2.3.4 The Effect of Strain Rate on SCC Susceptibility

The strain rate at the crack tip can account for the repeated plastic deformation that is needed at the crack tip in order for SCC to continue. Diegle and Boyd\(^{(191)}\) proposed that the rate of strain is either to promote repetitive film rupture or possibly to maintain (through enhance dissolution) a transition film of poor protective quality, which in turn facilitates crack initiation and propagation by a particular mechanism. Solomon et al. \(^{(192)}\), in a study of strain rate effects for stainless steel in MgCl\(_2\) solution, proposed that the rate determining steps for SCC are the formation of slip steps and a corrosion process on the slip steps at the slower strain rate and faster strain rate, respectively. Therefore, SCC is most severe when both of
these processes are equal to each other(193). Figure 37 presents
the effect of strain rate on elongation to fracture for Type 304
stainless steel in high temperature water(171)

2.3.5 Effect of Chloride Ions on SCC Susceptibility

The effect of chloride ions on SCC susceptibility is a
function of the chloride ion concentration and the dissolved
oxygen in the corrosive environment and of the material and
its heat treatment. Chloride ions promotes SCC of both annealed
and sensitized austenitic stainless steel in high temperature
water containing high oxygen. But, in high temperature water
containing low oxygen, chloride addition up to 100 ppm (2.8x10^{-3}M)
have no influence on SCC susceptibility. The effect of chloride
ions on the SCC behavior becomes more pronounced as the degree
of sensitization increases.

Changes in chloride concentrations appear to have little
effect on the threshold stress intensity value or crack propaga-
tion rate of low alloy high strength steels having yield strengths
exceeding 200 ksi (1380 MPa)(5). Figure 38 shows the effect of
sodium chloride concentration on time-to-failure of AISI 4120
steel. Most of the reduction of specimen life occurs in weaker
solutions containing approximately 0.5% sodium chloride. Sodium
chloride concentrations greater than about 20% may lead to rapid
corrosion and crack blunting.
Figure 39 Dependence of elongation to fracture on strain rate (171)
Figure 40 Effect of sodium chloride concentration on the time-to-failure (190)
3.0 EXPERIMENTAL DETAILS

In this section the experimental materials, test apparatus, and procedures are described. They are as follows: (1) test materials (the chemical composition and specimen preparation) (2) apparatus (once-through refreshed autoclave and the various parts of the system) (3) procedures (the general procedures and data analysis).

3.1 Materials

Throughout the experiment, ASTM A508 Cl.2 steel was the major material of study. Sensitized Type 304 stainless steel was employed to compare the results for the effect of flow velocity on SCC susceptibility.

Figure 39 is a schematic of a BWR. ASTM A508 Cl.2 steel is utilized for the nozzles and flange of the reactor. The steel used in this investigation was supplied by the Cann & Saul Steel Co., Royerford, PA, in the form of a 20 cm x 20 cm forging quality billet (Heat # 219763). The chemical composition and mechanical properties of the steel are given in Table 2. The certified chemical analysis by the company is compared with that of the ASTM specification.

A 1.2 cm thick slice was cut from the billet perpendicularly to the rolling direction. From this slice 1.2 cm x 1.2 cm bars were made. These were swaged into 0.635 cm diameter by 66 cm long rods. Each swaged rod was cut into half to produce two 33 cm long specimen blanks. The 1.27 cm gauge length of each specimen, Figure 40, was located 2.54 cm below the outer surface of the original
Materials of Construction
for a Typical Boiling Water Nuclear Reactor

Figure 41 A schematic of BWR
Table 2 Chemical composition, mechanical properties and heat treatment of ASTM A508 Cl.2 steel

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM Specifications</td>
<td>.27max</td>
<td>.50-.90</td>
<td>.025max</td>
<td>.025max</td>
<td>.15-.35</td>
<td>.25-.45</td>
<td>.50-.70</td>
<td>.05max</td>
</tr>
<tr>
<td>Mill-Analysis (Heat No. 219763)</td>
<td>.71</td>
<td>.012</td>
<td>.015</td>
<td>.23</td>
<td>.43</td>
<td>.81</td>
<td>.66</td>
<td>.04</td>
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</tbody>
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Mechanical Properties (at H.T.)

<table>
<thead>
<tr>
<th></th>
<th>Yield Strength (MPa (ksi))</th>
<th>Tensile Strength (MPa (ksi))</th>
<th>% Elongation (Min.)</th>
<th>% K.A. (Min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM Specifications</td>
<td>345 (50)</td>
<td>550-725 (80-105)</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>As-Tested</td>
<td>598 (86.7)</td>
<td>653 (94.7)</td>
<td>26.6</td>
<td>81.8</td>
</tr>
</tbody>
</table>

Heat Treatment

- Normalizing: 890°C, 1h, Air Cooling
- Austenizing: 860°C, 1h, Water Quench
- Tempering: 695°C, 6h, Furnace Cooling
- After Machining, Re-Tempering: 695°C, 2h, Furnace Cooling
Figure 42 Specimen geometry of constant extension rate test
billet in order to assure reproducible test material in the fracture region. Heat treatment was done under an atmosphere of flowing region. Prior to insertion into the furnace the specimens were degreased with acetone and polished with 600 grit SiC emery paper to minimize the effects of any residues on the specimen surface.

After heat treatment, the specimens were polished with 600 grit SiC paper to remove the oxide. The amount of removed material from the diameter of the specimen was less than 0.025mm. After polishing, the specimen was degreased with acetone and double distilled water prior to mounting in the autoclave for testing.

3.2 Apparatus

The constant extension rate tests were conducted in a once through refreshed autoclave system to determine the SCC susceptibility of the materials in high purity water. To examine the effect of fluid flow, a special flow channel was designed and mounted on the autoclave. A schematic of the test loop of the entire system is illustrated in Figure 43. The various components of the system are described below in detail.

3.2.1 Once-Through Refreshed Autoclave System

- Autoclave: the pressure vessel of 1 gallon (3.85 liter) capacity is made of Type 316 stainless steel and purchased from the High Pressure Products Corporation (see Figure 42)
- Cooling Tower: the colling tower contains approximately
Figure 43 Schematic diagram of test loop of once-through refreshed autoclave
13.7 cm of coiled 3.2 mm O.D. Type 316 s.s. tubing and was fabricated by the Davis Heliare Co.

- Back Pressure Regulator: this device allows for adjustment of the operating pressure of the system. It was purchased from the Tescom Corporation which was designed to operate at low flow rates and inlet pressures of up to 17.7 MN/mm².

- High Pressure Pump: the high purity water contained in the 95-liter storage tank enters the Yarway High Pressure positive Displacement Pump. The pump has a rated capacity 22 MN/mm² (3200 psi). The flow capacity is 3.6 liter/hr at the operating condition of 7.6 MN/mm² (110 psi). All of the parts exposed to the high purity water were made of Type 316 s.s. and diaphram is made of Teflon.

- Preheater: the preheater consists of an inner coil of approximately 18.3 m of 3.3 mm O.D. Type 316 s.s. tubing which has been coiled around the asbestos covered pipe. Two Briskeat heating jackets around the coiled tube. The upper heating jacket is controlled by a powerstat and the lower jacket is controlled by an on-off temperature controller. Each jacket is capable of producing 2500 Watts. The autocalve is surrounded by the Brisket heating jacket which is controlled by an on-off temperature controller. In order to control the temperature inside autoclave, an additional thermo couple, located inside the autoclave is
Figure 44: Type 316 stainless steel autoclave
another on-off temperature controller. The error range inside is less than 0.5 °C.

- Heat exchanger: the heat exchanger is attached to the entrance of the preheater to maintain the high temperature at the faster flow velocity in the study. It is made of Type 304 s.s.

- Special flow channel: in order to increase the flow rate around the specimen gauge section a special flow channel was designed and a schematic is shown in Figure 45. It is made of 304 s.s. rod stock. Careful machining is needed to prevent turbulent flow inside the channel. Prior to testing in the channel, the flow channel must be well-oxygenized in the high purity water to minimize contamination. Figure 46 shows the flow channel mounted on the autocalve.

3.2.2 Water Supplier

In order to simulate the actual BWR environment, high purity water having a resistivity in excess of 1M ohm-cm was needed. Table 3 presents the water chemistry of an actual BWR. This quality of water was achieved and maintained in the laboratory through the use of the three pieces of equipment:

- Barnstead Still: the stream from the University is passed through the Barnstead Still and the water obtained is equivalent to single distilled water having a resistivity of 578,000 ohm-cm

- Millipore Super Q system: single distilled water from the Barnstead still is passed through several ion-exchanger and filtration cartridges made by the Millipore Corporation. The
Figure 45  A special flow channel to increase flow rate
Table 3

Actual BWR Chemistry

Typical Operating Conditions: Boiling and Superheat (68)

<table>
<thead>
<tr>
<th>Operating Mode</th>
<th>Boiling</th>
<th>Superheat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Temperature of Fuel Element Wall, F</td>
<td>644-842</td>
<td>878-932</td>
</tr>
<tr>
<td>Maximum Coolant Flow Rate, lb/h</td>
<td>1540-2200</td>
<td>1320</td>
</tr>
<tr>
<td>Operating Pressure, psi</td>
<td>1420</td>
<td>1270</td>
</tr>
<tr>
<td>Coolant Temperature, F, at Channel Entrance</td>
<td>347</td>
<td>t_{sat}</td>
</tr>
<tr>
<td>Coolant Temperature, F, at Channel Exit</td>
<td>t_{sat}</td>
<td>698</td>
</tr>
<tr>
<td>Quality at Exit %,</td>
<td>2-25</td>
<td></td>
</tr>
<tr>
<td>Water Analysis,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Solids,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Evaporation,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ppm</td>
<td>1.5-3</td>
<td>0.6-1.1</td>
</tr>
<tr>
<td>pH</td>
<td>5.6-6.2</td>
<td>5.5</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.5-1.0</td>
<td>0.9</td>
</tr>
<tr>
<td>NO₃</td>
<td>0.1-0.7</td>
<td>0.1-0.15</td>
</tr>
<tr>
<td>Cl</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>CrO₄²⁻</td>
<td>0.05-0.020</td>
<td>0.015</td>
</tr>
<tr>
<td>Fe</td>
<td>0.05-0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>Ni</td>
<td>0.005-0.02</td>
<td>0.005</td>
</tr>
<tr>
<td>O₂</td>
<td>4.5-7</td>
<td>4.6</td>
</tr>
<tr>
<td>H₂</td>
<td>0.4-0.8</td>
<td>0.3-0.5</td>
</tr>
<tr>
<td>N₂</td>
<td>5-12</td>
<td>5-12</td>
</tr>
</tbody>
</table>
Millipore Super Q can produce high purity water free from ionic concentration up to a 18 M ohm-cm resistivity level, and free from microbiological contamination. The output flow rate of the unit is 1.5 liter/min. The unit consists of four cartridges and the functions are as follows: 1) Super-C cartridges (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 in a highly efficient mixed bed of strong acid and strong base resins that do not need regeneration) 3) Millipore MF cartridge (the last one of this unit which removes any microscopic particles or microorganisms that may have escaped retention by the preceding upstream elements).

The storage and transfer tank, after passing through the Millipore Q system, the water is stored in a 190 liter Type 316 stainless steel tank. A solenoid valve with a timer is attached at the entrance of the 190-liter tank to prevent a reverse stream and to provide water of constant resistivity at the 190-liter tank. The high purity water is transferred from the storage tank to a 95-liter Type 316 stainless steel mixing tank (Fig. 45). The oxygen concentration is controlled by bubbling a gas mixture of oxygen and nitrogen through a Matheson Gas proportioner. The gas mixture is bubbled into the mixing tank through a Teflon "fritte". When the proper oxygen concentration is achieved in the high purity water, the water is transferred into a final 114-liter Type 316 stainless steel storage tank. The supply of high purity water is automa-
Figure 46 A special flow channel mounted on the autoclave
Figure 47 Schematic Diagram - 95 liter Mixing tank
tically controlled as shown in Figure 48. The unit is activated as follows: 1) when the water level in the final storage tank is below the present level, the level controller activates a transfer pump and the water is transferred to the final storage tank from the mixing tank. 2) Similarly, the water is transferred from the storage tank to the mixing tank.

Three auxiliary control features were also designed into the control system. The first one is that an oxygen monitoring system 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 for manual filling of the mixing tank from the 190-liter storage tank.

3.2.3 The Constant Extension Rate Device

The constant extension rate device shown in Figure 49 was utilized in the investigation. The device is composed of the following components:

- A constant speed motor provides the necessary power for straining the specimen.
- A series of gear reducers transmits power from the motor to the specimen. There are four gear reducers. The first one is a variable reduction unit with ratio from 1:1 to 50:1. The second one has a fixed ratio of 900:1. The third one has a worm gear with a ratio of 60:1 which converts the rotary motion of the motor to a vertical motion which provides a method of straining specimen. The one is a shaft with 18
Figure 48 Schematic diagram - oxygen control and transfer system
threads per 25.4 mm which is driven by the worm and pinion gears. The combination of the various motor speeds and gear ratios makes it possible to achieve cross head velocities from $1.27 \times 10^{-5}$ mm/sec to $1.27 \times 10^{-3}$ mm/sec. The strain rate of each specimen is calculated as described in Appendix I.

3.2.4 Measurement of Corrosion Potential

During straining the corrosion potential of the specimen is monitored with Ag/AgCl internal and external reference electrodes as shown in Figures 50 and 51, respectively. The internal reference electrode was used for tests below 250°C in the beginning of the work, but later the external reference electrode was utilized due to the fact that it maintains a stable value at high temperature during the test period.

3.2.5 Measurement of the Specimen Load

During straining the specimen load is continuously monitored on a chart recorder. A calibrated load cell is utilized to determine the load on the specimen. The load cell is made by BHL Electronics is activated with a specific voltage and puts out a corresponding voltage in proportion to the applied load on the specimen. The output voltage from the load cell is fed into a single conditioner, made by Sensotec, where the signal is amplified, which is fed into a recorder made by the easternline Angus.

3.2.6 Measurement of the Solution Conductivity and pH

Periodically, the conductivity of the water was checked with a Beckman conductivity bridge and a Beckman Model 350
Figure 50 Schematic of internal Ag/AgCl reference electrode
Figure 51 Schematic of Ag/AgCl reference electrode
3.2.6 Measurement of the Dissolved Oxygen Content

There are four techniques available to determine dissolved oxygen content of the water (186). They are the Beckman Model 735 Dissolved Oxygen Analyzer, Indigo Carmine, Winkler and Modified Winkler Technique, and Chemets.

- **Beckman Analyzer**: this is composed of three compartments, read-out console, micro-pump, and sensor. The micro-pump provides a necessary flow rate of 4.2 cc/sec. The sensor consists of a gold cathode, a silver anode, a Teflon membrane, and 4N KCl as an electrolyte. As the high flow of solution impinges on the membrane, the dissolved oxygen diffuses through the Teflon membrane. This oxygen reacts with the solution to produce KOH and a small current which is proportional to the oxygen content. The amplified current is calibrated to give a signal. The unit is designed to operate in the ppb range, but it can be extended to about $3.1 \times 10^{-4} \text{M}$ of oxygen (10 ppm).

- **Indigo Carmine Technique**: in the low oxygen content regime less than $1.8 \times 10^{-4} \text{M}$ oxygen, this technique is applicable. Dissolved oxygen reacts with the indigo carmine solution to produce a progressive color range from yellow to green through red to blue and blue to green. The oxygen in the water is determined by comparison of color developed in the sample with color standards made up to present proper oxygen.

- **Winkler Technique**: this is applicable to water with more than $1.6 \times 10^{-7} \text{M}$ (5 ppb) of oxygen, and having low
concentrations of reducing and oxidizing materials. The sampling must take place in a specially prepared container. After the sample has been collected, the free iodine liberated which is almost equivalent to the oxygen in the sample, is titrated with thiosulfate using starch as an indicator. Chemets: it is a disposable glass ampoule manufactured by Chemetrics. Each ampoule contains a certain amount of a color forming reagent and it is vacumm sealed. Breaking the tip of an ampoule in the flowing solution causes the solution to enter into the ampoule and mix with the reagent. It is a kind of instant colorimetric technique. The advantages are that it is simple, instantaneous, and there is no need for correction.

In this investigation, the oxygen concentration of the water was determined first by the Beckman oxygen analyzer, and was double checked by the Chemets. Periodically, Winkler technique was used to determine the oxygen concentration of water.

3.3 Experimental Procedures

Most of the tests were conducted in the once-through refreshed autoclave. For the study of the effect of high oxygen concentration (> 59ppm) on SCC susceptibility, a static autoclave was used.

3.3.1 Static Autoclave Testing

The procedure for CERT in the static autoclave system is as follows: (1) the parts of autoclave exposed to the environment were degreased with acetone and rinsed with distilled water (2)
the proper amount of double distilled water is added to the autoclave; the specimen mounted in the autoclave head is electrically isolated from the autoclave with a Teflon washer and shrinkable Teflon in Fig. 52. A specimen holder is zirconia-coated zirconium to avoid a possible galvanic coupling; the autoclave is heated to the desired temperature set by the automatic temperature controller; the straining device is activated 4-6 hrs after the test temperature is reached (to assure that steady state conditions were established); following failure of the specimen, the autoclave is cooled off by a blowing fan to minimize the change of corrosion products formed on the surface of the specimen during the cooling period (approximately 1 hr); as soon as the temperature inside the autoclave reaches 100°C, the autoclave head is opened and the failed specimen, removed from the head, is placed in a desiccator for further examination. The oxygen concentration in the static autoclave is calculated as illustrated in Appendix II.

3.3.2 Once-Trough Refreshed Autoclave Testing

(1) The oxygen concentration is obtained by bubbling the desired gas mixture into the mixing and storage tanks; the interior of the autoclave is degreased with acetone and rinsed with distilled water; the autoclave is filled with purified argon and then with pure water containing the required content of oxygen by activating the pump; temperature controllers are set (5) system pressurised about 400psi to avoid vapor phase by
Figure 52 Electrical isolation of specimen on the interior of the autoclave
the back pressure regulator,(6) the straining device is activated 4 - 6 hours after the temperature is obtained,(7) after failure, the high pressure pump is turned off. The preheater and autoclave heater are also turned off, (8) same as (7) in the section 3.3.1.

3.3.3 Crack Initiation and Propagation Studies

In order to obtain an actual crack propagation rate some interrupted tests were conducted. At the desired test time the power and straining device were turned off and the specimen was disconnected from the load cell. After the specimen was removed from the autoclave, it was examined under an optical microscope and scanning electron microscope. If the crack was visible under the optical microscope(X30), the specimen was fractured by repeated bending in air. If a crack was not detectable under the optical microscope, it was assumed that the crack depth was equal to its length measured under the SEM.

Average crack propagation rate is calculated from the crack depth observed in the SEM fractograph divided by the time from the onset of yielding to fracture.

3.3.4 Flow Effect Study

The preparation of the specimen and experimental procedures were the same as described in the previous section. Since one aim of this work was to study the flow effect on SCC behavior, a special flow channel which provides a reasonably well-defined hydrodynamic state around the gauge section of the specimen was employed. This is shown in Figures 43 and 44. The average flow velocity was calculated by dividing the measured flow rate at the drain by the annular space around the gauge section of the specimen. The Reynolds
number was chosen as a parameter to characterize the flow inside the channel and was calculated for every flow rate from the following equation (1)

$$Re = \frac{\nu \cdot d}{\nu} = \frac{\nu \cdot d \cdot \rho}{\mu} \ldots \ldots \ldots \ldots (1)$$

where,
- $\nu$ = kinematic viscosity
- $\nu$ = the average flow velocity around gauge
- $\mu$ = absolute viscosity of the fluid
- $\rho$ = the solution density
- $d$ = the diameter of the gauge of the specimen

Numerical data for the kinematic viscosity, water density, and Reynolds (Re) number are given in Table 4. Since the maximum Re number employed in this test was less than 2100, the system appeared to be operating under the laminar flow regime for all flow velocities.

The measurement of the crack propagation rate was described in section 3.3.3. Another method of estimating the crack propagation rate was employed for tests in flowing water. The record of load with time for ASTM A508 Cl.2 steel showed distinctively separated kinks. Once the maximum load was passed (see Figure 53) the number of kinks was found to be equal to the number of striations seen on the crack surface (see Figure 54). Accordingly, the author assumed that each kink in the chart represented a crack arrest, and that the time between kinks was equal to the time for crack propagation between arrests. From this, the crack propagation rate can be easily and accurately calculated from the width of the striation as measured from SEM fractograph, and by dividing the width by
Table 4 Reynold's number calculations for different temperature–flow rate conditions

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>d cm</th>
<th>ρ (g)</th>
<th>μ (poise)</th>
<th>ν (cm²/sec)</th>
<th>V cm/sec</th>
<th>Re</th>
</tr>
</thead>
<tbody>
<tr>
<td>200°C</td>
<td>0.254</td>
<td>0.8628</td>
<td>1.6 x 10⁻³</td>
<td>1.85 x 10⁻³</td>
<td>9.2</td>
<td>1.2</td>
</tr>
<tr>
<td>250°C</td>
<td>0.254</td>
<td>0.794</td>
<td>1.38 x 10⁻³</td>
<td>1.74 x 10⁻³</td>
<td>4.3</td>
<td>618</td>
</tr>
<tr>
<td>288°C</td>
<td>0.254</td>
<td>0.735</td>
<td>1.22 x 10⁻³</td>
<td>1.66 x 10⁻³</td>
<td>4.3</td>
<td>658</td>
</tr>
</tbody>
</table>

* Value of flow rate in once-through refreshing system.

Figure 53 Load vs time curve for ASTM A508 Cl.2 steel tested in aerated pure water at 288°C (flow rate=7.6 cm/sec)
Figure 54 The fracture surface with crack arrest marks on ASTM A508 Cl.2 steel tested at 250°C in aerated high purity water (flow rate = 7.6 cm/sec)
the time that passed between corresponding kinks.

The origin of the fluctuation is not clearly understood but is suggested that inside the autoclave, where there is a \( \pm 1.5 \) C fluctuation in temperature, the flow rate increased as high as 11.3 cm/sec and caused a maximum 20 pound (9Kg) kink on the recorder sheet. Despite the fact that fluctuation was observed on the stress strain curve over the whole straining time, the crack arrest marks were not observed prior to the maximum stress, either because these marks could not be resolved by SEM fractography or the crack propagation rate was not affected by these fluctuations. Accordingly, it was only possible to establish the depth of the crack in the last period of crack growth.

3.3.5 The Effect of Strain Rate

Similar constant extension rate tests were conducted in the water containing 8ppm (2.5x10^{-4} M) of oxygen at temperatures from room temperature to 250 C for A508 steel at strain rates of \( 10^{-5} \) and \( 10^{-6} \) sec^{-1}. The time-to-failure (\( E_f \)) was employed to determine the SCC susceptibility, and SEM fractographs were taken for the calculation of the average crack propagation rate.

3.6 The Effect of Chloride Ions

CERT was utilized to examine the effect of chloride ions on the SCC susceptibility in the water containing 8ppm (2.5x10^{-4} M), 6ppm (1.7x10^{-4} M), 24ppm (6.8x10^{-4} M), and 30 ppm (8.5x10^{-4} M) of chloride ions (from NaCl) at
The time-to-failure (elongation-to-fracture) was used to determine the SCC susceptibility and the SEM was employed to examine the effect of chloride ions on the formation of the magnetite double layer.

3.3.7 Data Analysis

SEM, metallography, Auger Electron Spectroscopy (AES), and X-ray diffraction were employed to analyze the specimen. The SEM was the primary tool used in determining the type and extent of cracking that the specimens had undergone when subjected to the various environments. The fracture surfaces and side surfaces were examined at low (27 to 390 X) to high (X 4300) magnifications.

Metallography was conducted on the fractured specimen. The specimens selected were polished with 240, 400, and 600 grit SiC papers after cold mounting. After that, they were mechanically polished on a Syntron unit with 1 micron alumina-diamond paste, and then finally polished with 0.05 micron alumina powder. The specimens were etched with nital (5%) (95% methanol and 5% HNO₃).

Some selected specimens were examined by AES. In order to identify the corrosion products of the selected specimens, X-ray diffraction analysis was performed. Also EDAX was utilized to identify the elements of the corrosion products.
4.0 EXPERIMENTAL RESULTS

4.1 Preliminary Tests

Prior to conducting the main tests in the chosen environment, preliminary tests were done to characterize the specimen and to develop baseline data for CERT in air. Characterization included metallography, control tests in air, and CERT for the effect of cold-work prior to heat treatment.

ASTM A508 Cl.2 steel specimens were heat treated by austenizing, quenching, and tempering. The microstructure is tempered martensite as shown in Figure 53.

As described in section 3.2, the specimen was prepared by cold-swaging (79% cold reduction). It was necessary to examine the effect of this cold work prior to heat treatment in order to minimize data scattering. As illustrated in Figure 54, specimens with different amounts of cold work were tested in the water containing 59 ppm ($1.8 \times 10^{-3}$M) and 300 ppm ($9.3 \times 10^{-2}$M) of oxygen at 288 C. It was found that the SCC susceptibility was independent of the amount of cold work prior to heat treatment.

Results of CERT concerning the data scattering, showed that the data scattering band was relatively narrow for the specimens tested at temperatures up to 250 C, regardless of oxygen concentration, whereas, a wide band was observed at 288 C for the specimens tested in the water containing 8 ppm ($2.5 \times 10^{-4}$M) of oxygen. The detail will be discussed in section 4.2.3.
Figure 55 Photomicrograph of Tempered martensitic structure of ASTM A508 Cl.2 steel
Figure 56 Effect of cold work prior to heat treatment on the time-to-failure of ASTM A508 Cl.2 steel
The CERT was conducted in air to develop the baseline data which will be used to determine the SCC susceptibility of the specimen in a given environment. Those data are illustrated in Figure 57. The fracture surface has 100% dimple structure in air (ductile failure).

4.2 The Effect of Temperature and Oxygen on SCC Susceptibility

Average crack propagation rate and elongation-to-fracture (time-to-failure) were chosen as parameters to determine the SCC susceptibility of the materials to the environments. This section includes the results of the effects of temperature and oxygen.

4.2.1 The Combined Effect of Temperature and Dissolved Oxygen

The primary purpose of this investigation is to determine the effect of oxygen and temperature on SCC susceptibility for the A508 steel which experiences transient periods during BWR operation. Nominal stress vs time curves are given in Figures 57-60 for specimens tested in the high purity water having 8ppm, 1ppm, 0.1ppm, and 0.015 ppm of oxygen at temperatures ranging from 25 C to 288 C. One interesting feature to be noted is that fracture stresses of the specimens tested in above 200 C water containing 0.1ppm oxygen are different from those of the rest of the specimens tested in air and the water. For example, the fracture stresses of the specimens tested in water having 8ppm of oxygen at 288, 250, and 200 C are zero, 35Ksi (242MPa), and 68Ksi (468MPa), respectively.
ASTM A508 CL2 STEEL
\( \dot{\varepsilon} = 10^{-6} \text{ sec}^{-1} \)
Water = Air-Saturated High Purity Water, (8 ppm, \(O_2\))

Figure 5.7 Nominal stress vs time curves for tests carried out at \(\dot{\varepsilon} = 10^{-6} \text{sec}^{-1}\) in aerated water containing 8ppm oxygen
Figure 58 Nominal stress vs time curves for tests done in high purity water containing 1 ppm oxygen
Figure 59 Nominal stress vs time curves for tests carried out in high purity water containing 0.1 ppm of oxygen.
Figure 58 Nominal stress vs time curves for tests done in high purity water containing 0.015 ppm of oxygen
Figure 61 shows a dependency of elongation to fracture \( (E_f) \) on temperature. The time-to-failure of specimens at R.T. in water containing oxygen (regardless of concentration) are the same for those tested in air. In contrast to the results obtained at R.T., a substantial decrease in time-to-failure was observed above 100°C in water containing 1ppm and 8 ppm of oxygen. The elongation to fracture vs temperature curves for \( [O_2] \) = 1ppm and 8 ppm pass through minima at 250°C. In the presence of 0.1ppm of oxygen, the specimen failed by SCC at 200°C. At 100°C and 150°C, however, several small cracks were observed on the specimens. The average length of these cracks was about 50 to 100 μm. Below 0.1 ppm of oxygen no cracking was observed. It should be noted that at 100°C SCC occurred only for the specimen tested in water containing 1 ppm of oxygen; a similar result was reported in the literature(115) for the sensitized Type 304 stainless steel.

Figure 62 and 63 show that elongation to fracture and average crack propagation rate, respectively, vs oxygen concentration in high purity water at temperatures from 100°C to 288°C. These figures demonstrate that at all temperatures except at 100°C, the time-to-failure decreases, and hence, the susceptibility to SCC increases with an increase in oxygen concentration to 9ppm of oxygen. The results of the CERT for ASTM A508 Cl.2 steel are given in Table 5.
Figure 61 Elongation to fracture as a function of temperature

Figure 62 Elongation to fracture as a function of oxygen concentration
Average crack propagation rate as a function of oxygen concentration

Figure 63: Average crack propagation rate as a function of oxygen concentration
### Table 5: Experimental results for CERT specimens (A508)

<table>
<thead>
<tr>
<th>Temp.</th>
<th>O₂ concentration</th>
<th>tₚ (h)</th>
<th>tₚ/tₛ in air</th>
<th>OUTS (μm)</th>
<th>OUTS (RDI)</th>
<th>OUTS/OUTS in air</th>
<th>Ef (%)</th>
<th>PA (μm)</th>
<th>Average crack propagation rate μm/h</th>
<th>As-tested surface appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 ppm</td>
<td>74</td>
<td>1.00</td>
<td>653</td>
<td>94.7</td>
<td>1.00</td>
<td>26.6</td>
<td>31.8</td>
<td>Pit</td>
<td>reddish-yellow corrosion products around pits</td>
</tr>
<tr>
<td>0.015 ppm</td>
<td>71</td>
<td>0.96</td>
<td>669</td>
<td>97</td>
<td>0.97</td>
<td>25.6</td>
<td>78.6</td>
<td>64.1</td>
<td>Pit</td>
<td>black oxide film</td>
</tr>
<tr>
<td>0 ppm</td>
<td>64</td>
<td>0.24</td>
<td>635</td>
<td>92.1</td>
<td>0.99</td>
<td>23.0</td>
<td>70.2</td>
<td>3.8x10⁻¹⁰ SCC + Pit</td>
<td>dark-brown corrosion products (rough surface)</td>
<td></td>
</tr>
<tr>
<td>1 ppm</td>
<td>65.4</td>
<td>0.96</td>
<td>658</td>
<td>95.5</td>
<td>0.96</td>
<td>23.5</td>
<td>59.8</td>
<td>8.4x10⁻¹⁰ SCC + Pit</td>
<td>dark-brown corrosion products</td>
<td></td>
</tr>
<tr>
<td>0.1 ppm</td>
<td>68.8</td>
<td>1.00</td>
<td>637</td>
<td>92.5</td>
<td>0.93</td>
<td>24.0</td>
<td>72.0</td>
<td>black oxide film</td>
<td>black oxide film</td>
<td></td>
</tr>
<tr>
<td>0.015 ppm</td>
<td>66.9</td>
<td>0.97</td>
<td>654</td>
<td>95</td>
<td>0.95</td>
<td>24.0</td>
<td>72.0</td>
<td>black oxide film</td>
<td>black oxide film</td>
<td></td>
</tr>
<tr>
<td>0 ppm</td>
<td>55.4</td>
<td>0.82</td>
<td>593</td>
<td>86</td>
<td>0.95</td>
<td>19.9</td>
<td>46.6</td>
<td>1.35x10⁻⁹ SCC + Pit</td>
<td>dark-brown corrosion products + dark blue oxide film</td>
<td></td>
</tr>
<tr>
<td>1 ppm</td>
<td>61.6</td>
<td>0.87</td>
<td>597</td>
<td>61</td>
<td>0.91</td>
<td>22.2</td>
<td>41.0</td>
<td>1.1x10⁻⁹ SCC + Pit</td>
<td>dark-brown corrosion products + dark blue oxide film</td>
<td></td>
</tr>
<tr>
<td>0.1 ppm</td>
<td>70</td>
<td>1.00</td>
<td>671</td>
<td>97.5</td>
<td>0.98</td>
<td>25.2</td>
<td>64.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.015 ppm</td>
<td>71.3</td>
<td>0.93</td>
<td>689</td>
<td>100</td>
<td>1.00</td>
<td>25.1</td>
<td>70.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 ppm</td>
<td>35.1</td>
<td>0.49</td>
<td>638</td>
<td>92.5</td>
<td>0.92</td>
<td>12.6</td>
<td>24.5</td>
<td>5.8x10⁻⁹ SCC</td>
<td>dark-brown loose corrosive products + shiny dark-blue oxide film</td>
<td></td>
</tr>
<tr>
<td>1 ppm</td>
<td>47.6</td>
<td>0.62</td>
<td>671</td>
<td>97.5</td>
<td>0.98</td>
<td>17.1</td>
<td>18.7</td>
<td>3.2x10⁻⁹ SCC</td>
<td>dark-brown loose corrosive products + shiny dark-blue oxide film</td>
<td></td>
</tr>
<tr>
<td>0.1 ppm</td>
<td>65.5</td>
<td>0.85</td>
<td>683</td>
<td>100</td>
<td>1.00</td>
<td>23.5</td>
<td>49.2</td>
<td>9.5x10⁻¹⁰ SCC</td>
<td>grayish oxide film (fine crystalline structure)</td>
<td></td>
</tr>
<tr>
<td>0.015 ppm</td>
<td>70.3</td>
<td>0.93</td>
<td>689</td>
<td>100</td>
<td>1.00</td>
<td>25.1</td>
<td>70.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 ppm</td>
<td>27.0</td>
<td>0.38</td>
<td>562</td>
<td>81.5</td>
<td>0.98</td>
<td>10.0</td>
<td>27.4</td>
<td>1.25x10⁻⁹ SCC</td>
<td>dark-brown loose corrosive products + shiny black oxide film</td>
<td></td>
</tr>
<tr>
<td>1 ppm</td>
<td>38.2</td>
<td>0.52</td>
<td>641</td>
<td>93</td>
<td>0.93</td>
<td>13.0</td>
<td>16.2</td>
<td>6.5x10⁻⁹ SCC</td>
<td>dark-brown loose corrosive products + shiny black oxide film</td>
<td></td>
</tr>
<tr>
<td>0.1 ppm</td>
<td>72</td>
<td>0.97</td>
<td>655</td>
<td>95</td>
<td>0.95</td>
<td>25.9</td>
<td>70.8</td>
<td>greyish black oxide film (fine crystalline structure)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.015 ppm</td>
<td>72.2</td>
<td>1.00</td>
<td>637</td>
<td>92.5</td>
<td>0.93</td>
<td>26</td>
<td>99.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 ppm</td>
<td>39.5</td>
<td>0.59</td>
<td>587</td>
<td>85</td>
<td>0.88</td>
<td>14.2</td>
<td>33.5</td>
<td>1.5x10⁻⁸ SCC</td>
<td>dark-brown loose corrosive products + shiny black oxide film</td>
<td></td>
</tr>
<tr>
<td>1 ppm</td>
<td>51.0</td>
<td>0.72</td>
<td>568</td>
<td>82.5</td>
<td>0.83</td>
<td>18.6</td>
<td>16</td>
<td>1.65x10⁻⁸ SCC</td>
<td>dark-brown loose corrosive products + shiny black oxide film</td>
<td></td>
</tr>
<tr>
<td>0.1 ppm</td>
<td>72.2</td>
<td>1.00</td>
<td>637</td>
<td>92.5</td>
<td>0.93</td>
<td>26</td>
<td>99.7</td>
<td>greyish black oxide film (fine crystalline structure)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.015 ppm</td>
<td>72.2</td>
<td>1.00</td>
<td>637</td>
<td>92.5</td>
<td>0.93</td>
<td>26</td>
<td>99.7</td>
<td></td>
<td></td>
<td></td>
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Figures 64 - 67 show fractographs and side surfaces of specimens fractured in the high purity water containing various oxygen concentrations over the temperature range from 25°C to 288°C. The specimens which underwent SCC exhibit a transgranular mode of fracture with multiple secondary cracks. The mechanical fracture following transgranular cracking was ductile and showed a dimple morphology. The specimens tested in water containing 1ppm (3.1x10^{-5} M) and 8ppm (2.5x10^{-4} M) of oxygen at R.T., 100°C, and 150°C exhibited pitting corrosion. Transgranular SCC was observed in the above solutions at temperatures from 100°C to 288°C (for 1ppm), and from 150°C to 288°C (for 8ppm).

Figure 68 shows the number of cracks on the fracture surface as a function of temperature. It was found that, at 100°C and 150°C, cracks nucleate from pits (the number of cracks on the fracture surface is proportional to the number of pits on the surface), and that the number of cracks on the fracture surface was much higher at these temperatures than at higher temperatures. Pitting attack occurs most severely at 100°C and 150°C in water containing 8ppm (2.5x10^{-4} M) and 1ppm (3.1x10^{-5} M) of oxygen, respectively. In the lower oxygen contents (<1ppm; 3.1x10^{-5} M), no pitting was found.

Figure 69 shows the regions of different fracture modes as a function of temperature and dissolved oxygen concentration. The general crack morphology is a combination of TGSCC, pitting, and mechanical fracture. The dotted lines in the figure represent a combination of temperature and oxygen concentration during normal BWR startup operation in the Vermont Yankee Nuclear Power Plant.
Figure 64 The fracture surfaces of CERT specimens tested in high purity water containing 8 ppm of oxygen (a) R.T. (b) 100°C (c) 150°C (d) 200°C (e) 250°C (f) 288°C
Figure 65 The fracture surfaces of CERT specimens in high purity water having 1ppm oxygen
(a) R.T. (b) 100°C (c) 150°C (d) 200°C (e) 250°C (f) 288°C
Figure 66 The fine crystalline magnetite formed on the side of CERT specimen of Figure 67.

Figure 67 The fracture surface of CERT specimen tested at 200°C in high purity water containing 0.1 ppm of oxygen.
Number of Cracks On The Fracture Surface, N

<table>
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<th>100</th>
<th>150</th>
<th>200</th>
<th>250</th>
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<tr>
<td>Sites, ppm</td>
<td>8</td>
<td>1</td>
<td></td>
<td></td>
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</table>

Figure 68 The number of cracks on the fracture surfaces of CERT specimen as a function of temperature

Figure 69 Crack morphology of CERT specimens as a function of temperature and oxygen concentration
SEM examination of the oxide films formed on the steel under different experimental conditions were also made. It was found that oxide films formed at 200°C, 250°C, and 286°C in water containing 0.1 ppm($3.1 \times 10^{-6}$M) oxygen had a fine crystalline structure, similar to the outer layer of the Potter-Mann type double layer, in Figure 64. The film was composed of magnetite. The same results were obtained for the specimens tested below 0.1 ppm($3.1 \times 10^{-6}$M) of oxygen. The oxide film formed at 250°C in water containing 8 ppm($2.5 \times 10^{-4}$M) and 1 ppm($3.1 \times 10^{-5}$M) of oxygen was especially interesting. As can be seen in Figure 68(a), cone-shaped crystals, probably hematite, are present on the inner smooth magnetite film. These crystals have a diameter $\sim 100 \mu$m at the base and a height of $\sim 120 \mu$m. Figure 68(b) shows a crystal at a higher magnification. Cracks are seen to nucleate at these hematite crystals (Figure 68 a, c). Figure 68(d) shows the metal surface after descaling of (a) in Clarke's solution. The round spots (shallow depression) on the metal surface are the sites where hematite crystals were attached to the surface. Cracks are visible emanating from some of these depressions. As can be seen from the micrographs (Figure 68 e, f) the depressions have the same size as the base of the cone-shaped crystal. Neither crystal nor depressions apparently grow with time once a critical size is reached. The depression in Figure 68(e) was obtained after 12.5 hours when the SCC test was interrupted and the depression shown in Figure 68(f) was obtained when the specimen failed after 28 hours. In this case the well-defined crystalline magnetite was not observed as an outer layer of the double magnetite layer. It
Figure 70 SEM photographs of CERT specimens tested in high purity water containing 8 ppm of oxygen at 250°C
(a) as-tested surface appearance
(b) high magnification of (a)
(c) another formation of hematite
(d) after descaling in Clarke solution
(e) the depression observed after 12.5 hrs
(f) the depression across crack after 28 hrs
It is assumed that loosely attached hematite was formed instead of the crystalline magnetite.

In order to verify the identity of the cone-shaped crystals, X-ray diffraction analysis was performed by using Co-K\(\alpha\) radiation with an Fe filter. The sample was made by descaling the specimen with a knife. Accordingly, the corrosion products were found to be composed of hematite and magnetite. In fact, the corrosion products had a dark-brown color, but after removal of the loosely attached corrosion products, the oxide film had a shiny black color. Therefore, it is assumed that the outer layer including the cone-shaped crystal is made of hematite and the inner layer is magnetite.

The morphology of the cone-shaped crystal is indicative of the fact that these crystals were produced from a rapid precipitation process in the supersaturated condition.

The cross-section of the fractured specimen was examined under an optical microscope after the specimen was nickel plated and cold mounted. The results are presented in Figure 69. Above 200°C, depressions were observed, whereas pitting was found below 200°C in the oxygenated water (\(> 1\text{ppm} \times 3.1 \times 10^{-5}\text{M}\)). The shape of the hematite depression varied with temperature and oxygen concentration. For example, at 200°C, and with 8ppm (2.5x10^{-4} M) oxygen, the depressions are shallow, but wide. At 250°C, however, the depressions are narrow, but deep.

One of these depressions was examined with EDAX to identify a possible mechanism of the initiation of SCC. Figure 70 demonst-
Figure 71 Micrographs of the CERT specimens in pure water containing 8ppm of oxygen
(a) at 100 °C (b) 150 °C (c) 200 °C
(d) at 288 °C (e) 250 °C (f) 250 °C
Figure 72 EDAX spectrum at the depression
rates that manganese and sulfur were detected. Thus, second phase, non-metallic inclusion, MnS, could be the initiation sites for SCC.

4.2.2 The Effect of Dissolved Oxygen on SCC Susceptibility

The effect of dissolved oxygen on the SCC behavior of A508 steel in high purity water was studied at 288°C for oxygen concentrations of 0.015 ppm to 300 ppm. In Figure 73, the elongation to fracture, the average crack propagation rate are plotted as a function of electrode potential. As was expected, increasing the oxygen concentration to 8 ppm shortens the time-to-failure and hence, increases SCC susceptibility. However, a further increase in the oxygen content reverses the trend. The maximum SCC susceptibility coincides with the highest anodic current density on the anodic curve. The anodic curve is for a stationary deaerated solution. As can be seen in the figure, the two parameters, $t_f$ and $E_f$, did not always show the same susceptibility of the steel to SCC over the range of oxygen concentration.

Figure 74 shows SEM fractographs of a specimen tested at 288°C in water having 300 ppm oxygen. The high magnification fractograph, taken close to the initiation site and the periphery of the cracked area, shows the corrosion product to be hematite (Fig. 74). Three distinctive morphologies of corrosion products on the fracture surface are shown in Fig. 72(c, e, d): (c) well-defined cubic or octahedral magnetite (d) smaller octahedral magnetite.
Figure 73 Average crack propagation rate, time-to-failure and anodic polarization curve as a function of electrode potential.
Figure 74 The fracture surface of the specimen tested in 300 ppm of oxygen
(a) fracture surface
(b) higher magnification close to initiation site
(c) well-defined small octahedral magnetite
(d) less-well defined magnetite
hedral magnetite, (e) less well-defined magnetite. Obviously, the shape of the magnetite crystal on the fracture surface depends upon exposure time to the crack tip environment (or crack propagation rate). This is indicative of the fact that crack propagation rate is not constant for the CERT specimen (the details will be discussed in section 4.4.3). Therefore, when we use the average crack propagation rate as a parameter to determine the SCC behavior of the material, this result should be borne in mind.

Figure 73 shows photomicrographs of specimens tested in high purity water containing 59 ppm (1.8 x 10^{-3} M) and 300 ppm (9.1 x 10^{-2} M) of oxygen. In both cases, cracks are seen to nucleate from the depression underneath the cone-shaped hematite formation. The depression is smaller and shallower at 300 ppm (9.1 x 10^{-2} M) of oxygen.

The number and size of the cone-shaped hematite crystals are closely related to the SCC susceptibility of the steel. That is, they are present as the largest in both number and size for the specimens tested in the water containing 8 ppm (2.5 x 10^{-4} M) of oxygen. Above 59 ppm (1.8 x 10^{-3} M) of oxygen, a fairly uniform surface was obtained in the water without any distinctive localized corrosion products on the steel.
Figure 75 Micrographs of the CERT specimens tested in pure water containing (a) 59 ppm (b) 300 ppm of oxygen (at 288°C)
4.2.3 The Effect of Temperature on SCC Susceptibility

The effect of temperature on the SCC susceptibility was studied, in the temperature range of R.T. to 305°C, in high purity water containing 8 ppm (2.5x10^{-4} M) of oxygen. Time-to-failure was plotted as a function of temperature in Figure 76. The curves pass minima at 250°C (solid line: max. value) and 288°C (dotted line: min. value). As can be seen, a large scattering data band was obtained only at 288°C, where (A) and (B) represent maxima and minimum time-to-failure, respectively. The SEM micrographs for the specimens (A and B) at 288°C show a substantial difference in crack morphology and the number of cracks on the fracture surface. For specimen (A) only one crack nucleated and propagated to fracture, but for specimen (B) multiple cracks were observed on the fracture surface as shown in Figure 77. Additionally, more cone-shaped hematite crystals were formed for the specimen (B). This result agrees well with the polarization work. Figure 78 shows them for the unstressed cylindrical specimens, made from the fractured specimens, in 0.1 molal Na_2SO_4 solution at 288°C. Specimen (B) exhibits a slightly more active potential in the cathodic polarization. Around -100 mV_H, which corresponds to the corrosion potential of the specimen in aerated water, a decrease in anodic current density occurs for specimen (A). Both specimens show the same corrosion potential. The difference between these specimens is not clearly understood.

At higher temperatures (288°C) the number of the cone-shaped hematite crystals was reduced in comparison with those at the
Figure 76 Variation of time-to-failure on the test temperature.

ASTM A508 Cl.2 Steel
8 PPM Oxygen
CERT Specimen

Time To Failure, hr

0 50 100 150 200 250 300 350

Temperature, °C
Figure 77 The fracture surfaces of the CERT specimens tested in pure water containing 8 ppm oxygen at 288 C
(a) multiple cracks on the fracture surface (b) single crack on the fracture surface
Figure 78 Potentiodynamic polarization curves in 0.1 molal Na$_2$SO$_4$ of ASTM A508 Cl.2 steel at 288°C

ASTM A508 Cl.2 Steel
0.1 molal Na$_2$SO$_4$
50 mV/min
288°C

Deaerated solution
temperature. Namely, more uniform corrosion products were formed on the steel at the higher temperatures and hence, this apparently leads to a prolongation of initiation time.

4.2.4 Electrochemical Studies

Corrosion potential was monitored during the straining of the specimens. Figure 77 presents the corrosion potential of ASTM A508 Cl.2 steel in high purity water as a function of temperature and oxygen concentration. Corrosion potential behaves like an oxygen electrode, namely, a decrease in the oxygen concentration leads to a decrease of the corrosion potential. A significant decrease in the corrosion potential occurs in the range of the oxygen concentration between 0.015 ppm (4.7x10^{-7} M) and 0.1 ppm (3.1x10^{-6} M). As can be seen, increasing temperature results in a reduction of the corrosion potential for a given oxygen concentration.

Typical potential-time curves obtained during heating are presented in Figure 78. Under the deaerated condition, the corrosion potential changed slightly in the noble direction with an increase in temperature, and it settled down to about -600 mV H at 288 C. Under the aerated condition, initially, the corrosion potential changed in the less noble direction up to 75 C. This potential change is indicative of the active dissolution process of the specimen. Above 75 C, the corrosion potential shifted in the opposite direction. These potential-time curves were very reproducible when the heating rate of the autoclave was kept constant.
Figure 81 shows the corrosion potential measured during straining in the aerated high purity water. A slight increase with time in the corrosion potential occurs when crack propagation is mainly controlled by a mechanical factor: the rapid exposure of the newly formed surface at the crack-tip to the environment (see section 5.2).

Polarization curves are plotted in Figure 82 for 0.1 molal Na$_2$SO$_4$ solution (deaerated) at temperatures from 100$\,^\circ$C to 288$\,^\circ$C. The scan rate is 50 mV/min. In Figure 81, polarization curves obtained in the aerated and deaerated solutions are present for the unstressed specimens at 250$\,^\circ$C. Some interesting features are observed from these polarization curves. A transpassive region is seen to occur above 150$\,^\circ$C. A higher anodic current density is obtained at 200$\,^\circ$C in comparison with those obtained at 250$\,^\circ$C and 288$\,^\circ$C. Cathodic polarization curves are not noticeably changed at all the temperatures. The open circuit potential increases with a decrease in temperature.
Figure 79 Steady state corrosion potentials of ASTM A508 Cl.2 steel as a function of dissolved oxygen and temperature

Corrosion Potential of ASTM A508 Cl.2 steel in high purity water
Figure 60 Potential-time curves during heating-up period
Figure 81 corrosion potential monitored during the straining of specimens in aerated pure water
Figure 82 Potentiodynamic polarization curves of A508 steel in 0.1 molal Na$_2$SO$_4$.
4.3 The Effect of Fluid Flow on SCC Susceptibility

This section is divided into four subsections: stress-strain experiment, SEM observation, crack propagation measurement, and electrochemical studies. The material used in these experiments were A508 steel, 304 s.s., and 1020 steel.

4.3.1 Stress-Strain Experiment

Figure 83 shows the nominal stress vs time curves for A508 steel at the strain rate of $10^{-6}\text{sec}^{-1}$ in high purity water at various flow velocities and temperatures (250 and 288°C). Figure 84 exhibits similar data obtained for 304 s.s. at the strain rate of $1.5\times10^{-6}\text{sec}^{-1}$ at 250°C. In both cases the time-to-failure is found to increase with flow velocity. The stress at fracture for the A508 steel decreases with an increase in the flow velocity and temperature, whereas the fracture stress for 304 s.s. is close to zero regardless of flow velocities.

In Figure 83 the elongation to fracture for the materials is plotted as a function of flow rate, temperature, and oxygen concentration of oxygen, the elongation to fracture increases with increasing flow velocity for the specimens tested above 150°C. At 100°C, the time-to-failure was not affected by the flow velocity. The SCC susceptibility of the specimen tested in the water containing 0.1ppm at 200°C was found to be insensitive to the flow velocity.

The SCC susceptibility, regardless of materials, was
Figure 83 Nominal stress vs time curves of A508 steel in aerated water as a function of flow rate and temperature (250 and 288 °C).

Figure 84 Nominal stress vs time curves of 304 S.S. at a strain rate of $1.5 \times 10^{-6}$ sec$^{-1}$ in aerated water as a function of flow rate.
Figure 85 Elongation to fracture as a function of flow velocity
found to decrease abruptly at the flow velocity of 4.3 cm/sec (Re=500) and to exhibit a linear dependency on the flow velocity above 4.3 cm/sec. It is to be noted that, for A508 steel, a slope of a linear dependency of elongation-to-fracture on the flow rate becomes steeper with increasing temperature.

4.3.2 SEM Observations

Figures 86, 87, 88(a), and 88(b) show micrographs of the fracture and side surfaces of A508 steel cracked in high purity water having 8 ppm of oxygen at 288 C, 250C, 150C, and 100 C, respectively, at the different flow velocities. Figure 89 shows the fracture surface of Type 304 s.s.

The mode of cracking was transgranular for A508 and was intergranular for sensitized Type 304 s.s.

It was found that the number of cracks on the fracture surface of A508 steel diminishes with increasing flow rate, as shown in Fig.90, and show a linear dependency with both time-to-failure and flow velocity. In the case of Type 304 s.s., intergranular cracks started to grow only at two and three sites on the metal surface at all flow velocities.

Formation of the cone-shaped hematite crystals is diminished with increasing flow rate for specimens above 200C (for A508), however, a more uniform film was obtained in the flowing solution. The depression on the A508 steel
Figure 86 The fracture surfaces, side surfaces, and high magnification of the side surface of the CERT specimens tested at 250°C. 
(a) stationary (b) 4.3 cm/sec (c) 7.6 cm/sec (d) 9.2 cm/sec.
Figure 86 continued
Figure 87 The fracture, side and high magnification of side surfaces of the specimens tested at 288°C in pure water having 8 ppm of oxygen at the various flow rates

(a) stationary
(b) 4.3 cm/sec
(c) 7.6 cm/sec
Figure 88 Fracture surfaces and side surfaces of CERT specimens tested in pure water containing 8ppm of oxygen at the flow rate of 11.3 cm/sec
(a) at 100°C
(b) at 150°C
Figure 89 SEM fractograph of sensitized Type 304 stainless steel in the water containing 8 ppm of oxygen
Figure 90 Number of cracks on the fracture surface as a function of flow velocity and Time to failure for A508 steel in high temperature water
shows an important aspects of the effect of flow rate on the SCC behavior. Namely, increasing flow rate reduces the depth and diameter of hematite depressions where cracks nucleate.

At 100°C, the metal surface (A508) is covered with a yellow corrosion product (probably -FeOOH; goethite (169)) around the pits from the flowing solution, whereas in the stationary condition, a dark-brown thick corrosion product (hematite) was formed on the surface. The corrosion product on the Type 304 s.s. was not greatly affected by the flow velocity, but visually a shiny film was obtained in flowing water.

4.3.3 Crack Propagation Rate

The dependence of crack depth on time for sensitized Type 304 stainless steel and A508 steel was illustrated in Figure 91 and 92, respectively. Zero time corresponds to the time at which yielding is observed on the stress-strain curve. The data plotted in Figures 91 and 92 demonstrate that the crack depth (a) in both materials is a strong function of time (t) and also depends upon the fluid velocity. In both cases, the crack depth (a) was found to obey a function of the form

\[ a = c \cdot t^n \]  

in which both c and n depend on the flow rate. Numerical values for constant c and n are summarized in Table 6. These data demonstrate that for both alloys the exponent increases with flow, whereas the constant c decreases with flow rate. The initiation time for cracking was determined by extrapolating the log t vs log a relation in Figures 91 and 92.
Figure 91 Crack depth vs time for Type 304 S.S.
Crack Depth Profile

ASTM A508 Cl.2 steel
pure water (8 ppm O₂)
CERT specimen

Figure 92 Crack depth as a function of time
to an arbitrary chosen nucleus depth of 0.01 mm (10 μm). A plot of crack initiation time vs time-to-failure was found to be linear (see Figure 91), and the crack initiation time is observed to increase with increasing flow velocity (see Figure 92). The crack propagation rate is calculated by differentiating Eq(2) with time, t,

\[
\frac{d a}{d t} = c \cdot n \cdot t^{n-1} \quad \text{(3)}
\]

and is plotted in Figures 93 and 94 as a function of crack depth and time, respectively. These figures exhibit some interesting features of the effect of flow velocity on SCC behavior for the CERT specimens as follows:

- crack propagation rate is not constant, but increases exponentially with time during crack propagation
- flow velocity influences not only the time for crack initiation but also the crack propagation rate. The crack initiation time increases with an increase in flow rate and during the initial stage of crack propagation (see section 4.2.2) increasing flow velocity decreases the crack propagation rate, whereas at longer times the reverse effect is observed.

4.3.4 Electrochemical Studies

Corrosion potentials of both materials (A508 and 304 s.s.) were measured at temperatures of 100, 150, and 250°C by using an external Ag/AgCl reference electrode in the stationary and flowing conditions as shown in Figure 95. Polarization curves for ASTM A508 Cl.2 steel were obtained in 0.1 molal Na₂SO₄ solutions in the flowing and stationary conditions (11.3 and 8.6x10⁻³ cm/sec) at temperatures from
Figure 93 Crack initiation time vs time-to-failure for sensitized Type 304 s.s. and A508 steel.
Table 6 Numerical values for the \( n \) and \( c \)

<table>
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<tr>
<th>Flow Velocity</th>
<th>A508</th>
<th></th>
<th>304 s.s.</th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>( n )</td>
<td>( c )</td>
<td>( n )</td>
<td>( c )</td>
<td></td>
</tr>
<tr>
<td>8.6 ( \times 10^{-3} ) cm/sec</td>
<td>1.47</td>
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<td>2.03 ( \times 10^{-5} )</td>
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<tr>
<td>4.3 cm/sec</td>
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<td>7.6 cm/sec</td>
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<tr>
<td>9.2 cm/sec</td>
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<tr>
<td>11.3 cm/sec</td>
<td>6.48</td>
<td>1.65 ( \times 10^{-10} )</td>
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</tbody>
</table>

Figure 94 Crack initiation time as a function of flow rate for Type 304 s.s. and A508 steel
Figure 95 Crack propagation rate as a function of crack depth
Figure 96 Crack propagation rate as a function of time

- Type 304 stainless steel
- ASTM A508 Cl.2 steel

Flow affected zone for ASTM A508 Cl.2 steel
Flow affected zone for Type 304 stainless steel

Increasing flow velocity

Crack propagation rate (mm.hr)

Time, hr

10^0

10^1

10^2
100 C to 288 C in Figure 96 - 98. These curves exhibit the following general features:

- flow increase the corrosion potential by 20 to 30 mV in the positive direction at all temperatures for both materials.
- the polarization curves for Type 304 stainless steel are insensitive to flow velocity
- the anodic currents observed for ASTM A508 Cl.2 steel diminish substantially in the moving media

4.4. The Effect of Strain Rate on SCC Susceptibility

Constant extension rate tests were performed at a strain rate of $10^{-5}$ sec$^{-1}$ to examine the effect of strain rate on SCC susceptibility in high purity water containing 8 ppm ($2.5 \times 10^{-4} M$) of oxygen at temperatures from 25 C to 250 C. Figure 101 illustrates nominal stress vs time curves for tests carried out in aerated pure water. At this strain rate a decrease in time-to-failure occurred above 200 C. Figure 100 shows SEM photographs of the specimens fractured at the different temperatures. The specimen which underwent SCC exhibits a transgranular mode of fracture with multiple secondary cracks. In comparison to the specimens tested at the strain rate of $10^{-6}$ sec$^{-1}$, the number of cracks on the fracture surface has diminished as presented in Figure 103. The general crack morphology is a combination of TGSCC, pitting, and mechanical frac-
Figure 97 Corrosion potential as a function of temperature in the stationary and flowing conditions (materials: ASTM A508 steel and 304 s.s.)
Figure 98 Potentiodynamic polarization curves in the stationary and flowing conditions.
ASTM A508 Cl.2 Steel
0.1 molal Na$_2$SO$_4$
50 mV/min
Deaerated Solution

Figure 99 Potentiodynamic polarization curves of A508 steel in 0.1 Na$_2$SO$_4$ in the stationary and flowing conditions
Figure 100 Potentiodynamic polarization curves of A508 steel in 0.1 Na₂SO₄ solution in the stationary and flowing conditions.
Below 150 °C pitting and mechanical fracture were observed on the fracture surface, and cracks nucleate from pits. Above 200 °C TGSCC and mechanical fracture were found, and cracks nucleate from the cone-shaped hematite crystals.

The average crack propagation rate was plotted, in Figure 104, as a function of temperature and strain rate. It was found that an increase in the strain rate results in an increase in the SCC susceptibility (average crack propagation rate).

4.5 The Effect of Chloride Ions on SCC Susceptibility

Constant extension rate tests were conducted at a strain rate of $10^{-6}$ sec$^{-1}$ to examine the effect of chloride ions on SCC susceptibility in the aerated water containing 6 ppm ($1.7 \times 10^{-4}$ M), 24 ppm ($6.8 \times 10^{-4}$ M), and 30 ppm ($8.5 \times 10^{-4}$ M) of chloride ions at 250 °C.

Figure 105 shows the effect of chloride contamination on the nominal stress vs time curves. A substantial decrease in the time-to-failure is observed with increasing chloride ion concentration. The fracture stress increases with an increase in chloride ion concentration.

Figure 106 shows representative SEM fractographs. Results in the chloride solutions are summarized as follows:
- TGSCC is initiated from the cone-shaped hematite crystals in the 6 ppm ($1.7 \times 10^{-4}$ M) Cl$^-$ solution as shown in Figure 107(a). However, above 24 ppm ($6.8 \times 10^{-4}$ M) of Cl$^-$, cracks are initiated from smooth surface as shown in Figure 107.
ASTM A508 CL2 STEEL
\( \dot{\varepsilon} = 10^{-5} \text{ sec}^{-1} \)
Water = Air-Saturated High Purity Water, (8 ppm, O\(_2\))

Figure 101 Nominal stress vs time curves for tests carried out at \( 10^{-5} \text{ sec}^{-1} \) in aerated high purity water
Figure 102 Fracture surfaces of the CERT specimens tested in pure water containing 8 ppm of oxygen at the strain rate of $10^{-5}$ sec$^{-1}$. 
Figure 103 The number of cracks on the fracture surfaces of A508 steel at the strain rate of $10^{-6}\text{sec}^{-1}$ and $10^{-5}\text{sec}^{-1}$
Figure 104: Average crack propagation rate as a function of temperature at the strain rates of $10^{-6}\text{ sec}^{-1}$ and $10^{-5}\text{ sec}^{-1}$. 

ASTM A508-Cl.2 Steel in Pure Water (8 ppm O$_2$) CERT Specimen
(b) hematite formation is suppressed in solution having 24 ppm($6.8 \times 10^{-4}$ M) chloride ions, whereas below 24 ppm($6.8 \times 10^{-4}$ M) chloride ions large, crystalline, magnetite agglomerates are seen at initiation sites and at the periphery of the cracked area (see Figure 107a).

Small pores are visible between magnetite grains in Fig. 107(c). The presence of pores in the inner magnetite layer on the SEM photomicrograph indicates that diffusion of ferrous ions in the poric fluid may be the controlling factor in the formation of the magnetite double layer.

A well-defined magnetite double layer is observed on the steel tested in water containing above 24 ppm($6.8 \times 10^{-4}$ M) of chloride ions as shown in Figure 107(c,d).
Effect of Cl\textsuperscript{−} on the SCC Susceptibility

Figure 10.5 Nominal stress vs time curves of ASTM A508 Cl.2 steel in the oxygenated (8 ppm O\textsubscript{2}) water with chloride ions at 250°C.
Figure 106 Fractographs of A508 steel in water containing
(a) 6 ppm Cl⁻
(b) 30 ppm Cl⁻
Figure 107 SEM micrographs of ASTM A508 Cl.2 steel in the chloride solution at 250°C
(a) large, crystalline, magnetite agglomerates
(b) and (c) initial stage of the formation of inner magnetite layer
(d) fully developed magnetite double layer
5.0 DISCUSSION

This section is divided into five subsections. The first one considers the combined effect of temperature and oxygen on SCC susceptibility of ASTM A508 Cl.2 steel in high purity water. The effect of flow velocity on the SCC behavior for Type 304 stainless steel and A508 steel is discussed in the second section. The effect of strain rate and chloride ions on SCC susceptibility will be discussed in sections 5.3 and 5.4, respectively. Finally, some experimental difficulties are considered in the last subsection.

5.1 The Combined Effect of Temperature and Dissolved Oxygen

Localized corrosion processes usually occur on metals covered by oxide films. Therefore, the discussion concerning the pitting and stress corrosion cracking of ASTM A508 Cl.2 steel in pure water, as a function of oxygen concentration and temperature, will be combined with an analysis of the available information on composition and stability of the oxide film formed on carbon steels, in general in oxygenated systems at elevated temperatures.

At room temperature, the corrosion products formed on mild steel in oxygenated water are $\delta$-FeOOH and $\delta$-FeOOH + magnetite after short (hrs) and long (weeks) exposure periods, respectively. Fe(OH)$_2$ is also formed. At about 100°C, Fe(OH)$_2$ decomposes to Fe$_3$O$_4$ and H$_2$ and at about 200°C $\delta$-FeOOH dehydrates to form $\delta$-Fe$_2$O$_4$(124). On heating to 316°C, any Fe(OH)$_2$ or $\delta$-FeOOH generated by exposure of the cell to water at ambient temperatures is converted to magnetite(Fe$_3$O$_4$) within 24 hours. Also, at this...
temperature, any \( \alpha \) or \( \beta \)-FeOOH generated by room temperature exposure to \( \text{H}_2\text{O}_2 \) solution (i.e. to a high oxygen concentration) are converted to \( \alpha - \text{Fe}_2\text{O}_3 \) within 24 hours. These results were obtained by Strauss and Bloom (124) when iron oxides were heated in sealed platinum-lined nickel capsules.

Many workers report the formation of both magnetite and hematite (\( \alpha - \text{Fe}_2\text{O}_3 \)) on steel in water containing oxygen at elevated temperatures (123, 124, 166, 168-170) in spite of the fact that, according to equilibrium thermodynamic data, only \( \alpha - \text{Fe}_2\text{O}_3 \) should be stable. However, under certain conditions, single-layer hematite film can be formed. For example, Ruther and Hart (138) found that only hematite formed on carbon steel in water containing 130 ppm (3.25 \times 10^{-2} M) of oxygen. X-ray diffraction analysis (123) of the films formed on plain carbon steel in pure water containing 30 ppb (9.1 \times 10^{-7} M) of oxygen at 125 C and 288 C show that they are composed of magnetite. A magnetite film is also produced at 50 C and 100 C water containing 8 ppm (2.5 \times 10^{-4} M) of oxygen. On the other hand, the films formed at 175 C and 288 C in water containing 8 ppm (2.5 \times 10^{-4} M) of oxygen consist of two layers: an inner layer of magnetite next to the steel and an outer layer of hematite (123). From the literature data quoted above, it is apparent that at high oxygen concentrations (high anodic potentials) and at moderate temperatures (175 - 300 C) hematite is more stable than magnetite, which is in accordance with thermodynamics data for Fe-H\(_2\)O systems at elevated temperature (167).

In this work two regions of temperature might be distinguished
with regard to the nucleation of the transgranular cracks. Accordingly, at temperatures of 100°C and 150°C cracks nucleate only from corrosion pits (see Figure 59). On the other hand, at temperatures of 200°C, 250°C, and 288°C cracks apparently nucleate from the smooth metal surface or from shallow depressions that are present on specimens that were oxidized at these higher temperatures. These depressions are quite different in morphology from the pits that form at lower temperatures. The different susceptibilities to pitting and SCC can be explained by the different properties of the film. At lower temperatures, a protective magnetite film is present on the metal surface. Hence, the metal surface can be attacked only at weak spots, such as regions that are adjacent to nonmetallic inclusions (MnS) and carbides precipitates. As a result, dissolution occurs chiefly at these sites, developing pits. Manganese sulfide dissolves at high anodic potentials with the formation of protons thereby causing local acidification of the solution and preventing repassivation of pits. Additional reactions which would be expected to occur at pits (or at the crack tip during crack propagation) are as follows:

\[
\begin{align*}
\text{Ni} & = \text{Ni}^+ + 2e^- \\
\text{Ni}^+ & + \text{H}_2\text{O} = \text{NiO} + 2\text{H}^+ \\
\text{Me} & + \text{S} + 2\text{H}_2\text{O} = \text{HS}^- + \text{H}^+ + \text{M(OH)}_2 \\
\text{P} & + 2\text{H}_2\text{O} = \frac{1}{2}\text{H}_2 + \text{H}^+ + \text{H}_2\text{PO}_2^-
\end{align*}
\]

All of these reactions tend to lower the pH within the pits (or crack tip). Therefore, cracks nucleate from the pits (or form the base of the hematite crystals). The crack propagation process
may be suggested by the following steps:

(1) the combination of tensile stress and strain rate results in the rupture of the protective oxide film at the bottom of pits (or at the base of hematite crystal). In the case of A508 steel magnetite is the major protective oxide.

(2) a dissolution occurs at the exposed base metal until the dissolution is impeded by the presence of an oxide at the crack tip.

(3) successive film rupture, dissolution and repassivation events result in macroscopic SCC.

At 100°C, the fact that TGSCC was observed only for the specimen tested in water having 1ppm of oxygen can be explained in terms of repassivation kinetics and dissolution rate. As shown in Figures 67 and 77, the higher anodic potential is indicative of the higher dissolution rate due to the larger driving force of the oxygen concentration cell. Therefore, passivation is suppressed such that only pitting is favorable in the process (8ppm). However, at the lower oxygen content (1ppm), a reduction in the corrosion potential causes an increase in a repassivation kinetics, and hence SCC occurs. At low oxygen concentrations (<1 ppm), a protective magnetite formed on the steel (or a rapid repassivation kinetics) did not allow pitting to occur.

At high temperatures, hematite "christmas tree (cone-shaped)" were found to grow on top of the base magnetite layer. The mechanism of formation of $\alpha$-Fe$_2$O$_3$ is not well known (145), but the morphology of the deposit suggests that hematite ($\alpha$-Fe$_2$O$_3$) forms
via a soluble intermediate. Also, $\gamma'$-Fe$_2$O$_3$ is known to transform to $\alpha$-Fe$_2$O$_3$ at temperatures above 250 °C (145) so that it is possible that maghemite($\gamma'$-Fe$_2$O$_3$) is also an intermediate in the formation of hematite at elevated temperatures. The fact that the Christmas tree-shaped crystals of hematite, which form on top of the magnetite film, subtend small depressions suggests that the hematite nucleates at spots which are capable of supplying dissolved iron of sufficiently high concentration to exceed the local equilibrium solubility of hematite. The nature of these "weak" spots is not known, but presumably involve chemical inhomogenities on the metal surface. Based on these assumptions the mechanism for the cone-shaped hematite crystal is proposed below (see Figure 106).

1. A microporic inner magnetite layer is formed through iron dissolution competing with magnetite formation at the transient surface of the steel. Underneath the magnetite layer weak spots were formed, probably, around the nonmetallic inclusions (MnS) or carbides.

2. Preferential attack occurs at these weak spots and an acceleration of microdissolution causes local film break-down of the protective magnetite layer.

3. Auto-catalytic processes accelerate local acidification which leads to a large dissolution of the base metal and to increased solubility of the magnetite (145). Thus, a high concentration of the soluble ferrous ions are available and can be transferred into the bulk solution through the pores. Both depressions and
hematite crystals start to grow

(4) The ferrous ions may be transported a finite distance. The distance of transport of the ferrous ions prior to oxidation depends on the oxygen concentration gradient. The ferrous ions would be oxidized to ferric ions in the high concentration of oxygen in the bulk solution. Rapid precipitation of ferric ions in the oxygenated water results in the macroscopic cone-shaped hematite crystals. It is assumed that precipitation of magnetite is favored thermodynamically inside the wall of the cone-shaped crystal (low pH, oxygen). Therefore, it is supposed that a steady state (no growth with time) is developed when the local equilibrium solubility of the magnetite inside the crystal exceeds the concentration of the supplying dissolved Fe(II) ions, and hence the precipitates stifle the passage of the ferrous ions. The distance of transport of ferrous ions depends not only on the oxygen concentration gradient, but also on floe conditions. In the once-through refreshed autoclave system, which has a flow rate of $8.6 \times 10^{-3} \text{cm/sec}$, some hematite were formed on the inner magnetite layer apart from the cone-shaped crystals due to this flow as illustrated in Figure 111.

In the case of higher temperature ($> 288 \text{C}$) and higher oxygen concentrations ($> 8 \text{ppm}$), the metal surface is more uniformly covered with hematite and the localized hematite formation is reduced. The results agree well with the observation that increasing oxygen concentration results in a reduction of the anodic current density.
bulk solution

(1) Magnetite inner layer formed by the interconnecting poric diffusion of ferrous ions. Weak spots formed during the heating-up period around inclusions or carbides

(2) Microcrevice around the weak spots leads to cause break-down of protective magnetite inner layer

(3) The passage of ferrous ions is easier by the local dissolution of the magnetite film. The depression grows and hematite deposits on the magnetite layer

(4) A steady state is reached when the local equilibrium solubility of the magnetite inside the hematite crystal exceeds the concentration of the Fe$^{++}$ ions.

Figure 108 A schematic of proposed model of the formation of the cone-shaped hematite crystal
on the polarization curve. Thus, this apparently leads to a prolongation of the initiation time and substantially the SCC susceptibility is diminished. For the mechanism of the uniform hematite it is suggested that the soluble ferrous ions, that diffuse out through the poric fluid are oxidized to ferric ions on encountering oxygen in the bulk solution, and deposit on the magnetite inner layer (Fig. 112).

The interesting result in Figure 67, in which the SCC took place at 200°C in pure water containing 0.1 ppm ($3.1 \times 10^{-6}$) of oxygen, is explainable in terms of corrosion potential and oxide film properties. At 200°C, the corrosion potential located in the transpassive region and the anodic current density are higher than those obtained at the other temperatures. In SEM photomicrographs a well-defined, crystalline, magnetite double layer was observed. It is assumed that the solubility of the protective magnetite film and repassivation kinetics at the crack tip may be compatible to cause crack advancement. Above 200°C, a more protective magnetite (or possibly faster repassivation kinetics) prohibits film break-down, and subsequently, the material exhibits immunity to SCC. Below 200°C no pitting was observed and, therefore, the material exhibited only mechanical fracture. It is not reasonable to explain this on terms of an activation enthalphy basis since the average crack propagation rate consideration for the CERT specimen is too rough to be applicable to this material.
5.2 The Effect of Fluid Flow on the SCC Susceptibility for ASTM A508 Cl.2 steel and Sensitized Type 304 Stainless Steel in Pure Water

The results obtained in this study clearly show that an increasing flow velocity significantly increases the time-to-failure of both steels as determined by using the CERT technique. It is generally recognized that a time-to-failure can be divided into two components: an initiation time and a time for crack propagation. The incremental increase in the time-to-failure with each increase in flow velocity is found to be equal to the corresponding increase in the crack initiation time.

The diminished susceptibilities of the steels to cracking with increasing flow velocity can be attributed principally to a delay in crack initiation at the metal surface. As the flow rate increases, it is more and more difficult to generate the conditions necessary for crack initiation; namely, the agglomeration of loose corrosion products in weak spots on the metal surface, thereby permitting the accumulation of aggressive corrodents. Hydrolysis processes cause local acidification of the solution, which leads to metal dissolution. The number of cracks that propagates during straining is observed to decrease with increasing flow velocity (see Figure 88), because only the most susceptible spots on the metal surface are able to nucleate cracks under the less favorable condition which occurs in moving fluid media.

In the case of sensitized Type 304 stainless steel, the nucleation and growth of the cone-shaped oxide deposits is not observed as it is in the case of ASTM A508 Cl.2 steel. In the latter case,
cracks have been observed to nucleate from beneath the oxide deposits (see section 5.1). In the case of sensitized Type 304 s.s., the oxide film formed at the grain boundaries is thicker, more porous, and hence, less protective than that found on the exposed grains. Accordingly, accelerated corrosion occurs at the emergent grain boundaries thereby leading to the local build-up of aggressive species and to the acidification of the corroded grain boundary region. In both cases, crack nucleation probably involves a mass transfer process and/or a quiescent local environment for the appropriate conditions to develop. Fluid flow is expected to mitigate against the development of a local quiescent environments, and increased mass transfer may delay the formation of porous deposits, which in turn lead to the formation of occluded cells by decreasing the local degree of supersaturation.

The explanation advanced above is substantiated by the observed polarization behavior of the steels (see Figures 96 - 98). Fluid flow is seen to substantially reduce the anodic current density for ASTM A508 Cl.2 steel at high anodic potentials, regardless of temperature. This indicates that flow promotes the formation of more protective, less porous, oxide on the metal surface which is likely to exhibit a lower susceptibility to local break-down (crack initiation).

In the case of sensitized Type 304 stainless steel, the anodic polarization curves are almost independent of flow velocity at all temperatures, but the corrosion potential increases with velocity due to an increase in the oxygen supply to the metal surface. The
present study has also demonstrates that the crack propagation rate is not constant but increases exponentially with time as the crack propagates through the alloy matrix. Furthermore, the slope of $\log(\frac{da}{dt})$ vs $\log(a$ or $t$) becomes larger with an increase in the flow rate. This indicates that increasing flow velocity decreases the crack propagation rate during the initial stages of cracking, but that the crack propagation rate increases with flow velocity at the longer times.

Based on these data the effect of flow velocity on the crack propagation rate can be rationalized. At the initial stage of crack propagation ($<40 \mu m$ for ASTM A508 Cl.2 steel and $<15 \mu m$ for sensitized Type 304 stainless steel) as shown in Figure 104, physical and electrochemical factors seem to predominate in determining the crack propagation rate. That is, the flow mitigates against the local acidification. Consequently, SCC susceptibilities diminished during the initial stages of crack propagation. However, as the crack moves deeper a mechanical factor becomes increasingly predominant in determining the crack propagation rate. Because the crack initiation time increases with flow velocity (see Figure 92), and since the stress at crack initiation is also a linear function of initiation time (see Figure 107). The higher rate of crack propagation at higher flow velocity is due to the fact that the stress at initiation and hence the stress intensity at the tip of the growing crack increases as the initiation time is enhanced. In addition, the effect of strain rate is superposed on the SCC susceptibility for ASTM A508 Cl.2 steel because the number of cracks on the frac-
ture surface (proportional to the number of initiation sites on the specimen surface) diminishes with an increase in flow velocity; that is, the higher strain rate at the crack tip in the flowing solution leads to an increase in the crack propagation rate after the initial stage of propagation.

A significant difference exists between the behavior of Type 304 stainless steel and A508 steel with regard to the stress at fracture. The stress at fracture for Type 304 stainless steel is close to zero regardless of flow velocity, but that for the A508 Cl. 2 steel decreases with increasing flow velocity. It appears that in the case of A508 steel this phenomenon is a consequence of the number of cracks on the fracture surface. As previously noted, the stress at fracture for A508 steel decreases with increasing flow velocity, and becomes lower with a decrease in the number of cracks (see Figure 108). When the number of cracks is higher, the cross section of the specimen is more uniformly attacked by cracks (see Figure 84), than when there are few cracks (see Figure 84). The shape of the unattacked surface is different in the two cases: round in the first case, but a thin and irregular rectangle in the second case. The fact that the fracture stress is lower in the first case is probably related to this difference in the shape of crack-free regions.
Figure 109 Stress at crack initiation vs crack initiation time

Figure 110 Fracture stress vs number of cracks for A508 steel
Figure 111 Hematite formed some distance from the cone-shaped hematite

Figure 112 Uniform hematite formation in high oxygen concentration
5.3 The Effect of Strain Rate on SCC Susceptibility

Despite of the paucity of data, it is seen that the crack propagation rate increases with an increase in the strain rate. At high strain rate, the rate of film rupture is so rapid that the crack tip is almost film free during straining the specimen, or that a transition film of poor protective quality is maintained or the crack tip. Therefore, these effects could possibly cause a high dissolution rate only at the crack tip and less lateral dissolution, and hence the crack propagation rate increases with increasing the strain rate.

5.4 The Effect of Chloride ion concentration on SCC Susceptibility

Localized corrosion is accelerated for steels in solution containing oxygen and chloride ions. This is due to an auto-catalytic effect. In the present investigation oxide film formation on steels in the chloride solution, at elevated temperature, exhibits an interesting feature-cracks nucleate from localized corrosion products (see section 4.2). Chloride ions seem to contribute to the formation of oxide film and to the dissolution kinetics. The role of chloride ions on SCC is summarized as follows: suppression of the formation of "weak spots" in the inner magnetite layer; an increase in the dissolution rate on the metal surface in the chloride solution caused the surface to be covered with a more uniform oxide film. This oxide film formed during heating-up period of autoclave. Chemical inhomogeneity in the inner smooth magnetite layer, probably resulting from the phase transformation of the oxides during the heating-up period, may be prevented by the high dissolution rate.
A similar result was obtained by Castle and Mann (138) in a study of the mechanism of formation of a porous oxide film on steel; that is, the two-layer oxide on steel was obtained due to a higher dissolution rate in the early stages of oxidation by agitating the specimen coupon. Local acidification is accelerated at the crack tip in the presence of chloride ions. This leads to a slowing down of the repassivation kinetics (or an increase in the dissolution rate).

The time-to-failure was not changed significantly in the water containing less than 6 ppm (1.7 x 10^{-4} \text{M}) chloride ions. This is due to a trade-off between a higher dissolution rate (or faster crack propagation rate when both dissolution rate and repassivation kinetics are compatible for crack advancement) and lower probability for formation of the cone-shaped hematite crystals (which leads to a prolonging of initiation time). However, as the chloride ion concentration increases, in spite of the fact that cracks nucleate from the smooth metal surface and not from the cone-shaped hematite crystal, the oxide film becomes less protective, and hence the incubation time for cracking is shortened. Thus, SCC susceptibility increases with increasing chloride ion concentration above 24 ppm (6.8 x 10^{-4} \text{M}).

The formation of large, crystalline, magnetite at the initiation site and at the periphery of the cracked area of the specimen in the chloride solution appears to be attributed to the following facts: the presence of chloride ions, as mentioned above, increases the dissolution rate at localized spots, and hence, the
amount of soluble ferrous ions available to be oxidized is increased. The solution within a crack has a much lower potential and pH for tests in the chloride solution, that is, magnetite formation is thermodynamically favored around the initiation site and the cracked area instead of the formation of hematite in oxygenated pure water.

The fact that the fracture stress increases with increasing chloride concentration suggests rapid corrosion. Additionally as mentioned in the section 5.2, the shape of the unattacked surface is round in the chloride solution (above 24 ppm); that is, with an increase in chloride ions a more uniform attack occurred around the fracture surface.

5.5 Experimental Difficulties

The experimental difficulties, load measurement and oxygen consumption in the refreshed autoclave, are discussed below.

5.5.1 Load Measurement

There is difficulty in determining the effect of the Teflon gland in the Conax fitting on the frictional resistance of the pull rod. This frictional force is a function of the test temperature and system pressure. The maximum friction was less than 5% 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 these reasons, the load correction due to friction has been neglected. The decision to neglect the friction does not affect the overall results.
5.5.2 Oxygen Consumption in the Autoclave

Another problem in this investigation was the accurate measurement and control of oxygen concentration within the autoclave. The control of oxygen content was accomplished through the use of a gas proportioner and automated control equipment. The problem concerning control of the dissolved oxygen concentration of the system occurs within the autoclave at temperatures above 200 °C. The autoclave system used in this experiment was made of Type 316 stainless steel. The oxygen consumption problem was 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.
6.0 CONCLUSION AND SUMMARY

The important findings of this investigation are listed below:

(1) ASTM A508 Cl.2 steel undergoes transgranular SCC in pure water containing 1 ppm($3.1 \times 10^{-6}$ M) and 8 ppm($2.5 \times 10^{-4}$ M) of oxygen over the temperature range of 100 to 288 C.

(2) In water containing 0.1 ppm($3.1 \times 10^{-7}$ M) of oxygen, transgranular SCC occurs only at 200 C.

(3) Pitting corrosion occurs in pure water containing 1 ppm($3.1 \times 10^{-6}$ M) and 8 ppm($2.5 \times 10^{-4}$ M) of oxygen at 100 and 150 C. Transgranular cracking nucleates from corrosion pits.

(4) At the same concentration of oxygen in water, transgranular SCC occurs in the absence of pitting at 200 to 288 C but nucleates at the hematite crystals which form on the base protective films at sites of high local dissolution.

(5) The susceptibility to SCC as measured by time-to-failure increases with increasing oxygen concentration but exhibits a maximum as a function of temperature at 250 C.

(6) The time-to-failure of both A508 steel and Type 304 stainless steel in oxygenated water at 250 C, as determined by using the constant extension rate test technique, increases with increasing fluid flow velocity. The longer failure times are attributed mainly to an increase in the crack initiation time.

(7) The number of cracks observed on the fracture surface of ASTM A508 Cl.2 steel in this high temperature environment was found to decrease with increasing flow velocity. In the case of sensi-
tized Type 304 stainless steel, cracks nucleate from only two or three sites on the metal surface regardless of flow velocity.

(8) The rate and kinetic parameters for crack propagation as observed during constant extension rate tests, are a function of the initiation time, and hence, of the stress at crack nucleation. The increased stress at nucleation gives rise to higher crack propagation rates. It appears that the crack propagation rate in these two steels in oxygenated water at elevated temperatures is determined primarily by mechanical factors, particularly during the latter stages of failure.

(9) In solutions with an oxygen concentration above 8ppm (2.5×10^{-4} M), the SCC susceptibility was reduced due to the formation of a more uniform hematite film on the metal (this leads to a prolongation of initiation time).

(10) An increase in flow velocity leads to a decrease in the anodic current density regardless of test temperature for ASTM A508 Cl.2 steel (which reduces the formation of localized corrosion products: cone-shaped hematite crystal). However, the anodic current for Type 304 stainless steel is insensitive to the flow velocity.

(11) The SCC susceptibility is increased with increasing strain rate.

(12) The size of the magnetite crystals in the chloride solution is larger than that in the pure water for ASTM A508 Cl.2 steel.

(13) Chloride ions had little affect on the SCC susceptibility of ASTM A508 Cl.2 steel at 250 °C in the oxygenated water containing less than 6ppm (1.7×10^{-4} M) of chloride ions, but the time-to-failure
decreases with an increase in chloride ion concentration above 6 ppm (1.7x10^{-6} M)

In addition to these conclusions drawn from this investigation, several suggestions for areas which require further investigation were developed:

- In the field, actual flow velocities are in the order of a few meter per second. Therefore, it is necessary to conduct tests in the turbulent flow regime.
- The effect of solution conductivity, pH, and potential on the SCC susceptibility of both Type 304 s.s. and A508 Steel need to be determined.
- The environmental influence (pH, potential, oxygen, temperature) on the corrosion fatigue resistance has not been investigated.
- The effect of pre-film on the A508 steel on the SCC susceptibility is needed to explain the role of oxide film in the SCC behavior.
- Corrosion rate measurements should be investigated by using coupon specimens.
- Pitting corrosion is severe around 100°C. The AC-impedance technique using the transmission line model could be applied for determining the kinetics of pitting corrosion.
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APPENDIX I Calculation of Strain Rate(68)

The constant strain rate device consists of a variable speed electric motor, a 900:1 gear reducer, a variable gear reducer, a worm reduction gear(60:1), and a threaded shaft (18 threads/in). With this device the extension rates can be varied from $5 \times 10^{-7}$ to $5 \times 10^{-5}$ sec$^{-1}$. A sample strain rate calculation is shown below.

Motor speed Reduction gear Variable Ratio Gear reducer Worm gear gear reducer gear reducer (Rev/min) x (16/12) x (1/30) x (1/900) x(1/60)

Threaded shaft of sample

x (1/18) x (1/60) x (1/0.5)

= strain rate (in/in/sec)

A motor speed of 656 RPM yields a strain rate of $10^{-6}$ sec$^{-1}$
APPENDIX II Calculation of oxygen concentration in the static autoclave

The calculation of dissolved content of the water in the static autoclave at elevated temperature and pressure is shown below for one 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 of oxygen at the beginning of the experiment. Therefore, the total weight of oxygen in the autoclave is:

\[
3000 (g) \times (7 \times 10^{-6}) + 2 (l) \times 0.21 \times 273/293 \times 32/22.4 \text{ gmol/lmol} = 0.58 \text{ g}
\]

The volume of water after heating to 286 C is:

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

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 (kg/cm^2)

Water can contain 0.56 ml O_2/g H_2O (800 ppm) at 286 C under an oxygen pressure of 7.1 kg/cm^2. In the case of deaerated water, placing \( C_{O_2} \) (ppm) for the oxygen concentration at 286 C, the total oxygen balance in the autoclave is:

\[
3000 \times C_{O_2} \times 10^{-6} + (5-4.1) \times C_{O_2} / 800 \times 7.1 / 1.03 \times 273/559 \times 32/22.4 = 0.58
\]

Therefore, \( C_{O_2} = 69 \text{ ppm} \)