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ENVIRONMENTALLY - CONTROLLED CRACK GROWTH RATE OF TYPE 304 STAINLESS STEEL IN HIGH TEMPERATURE SULFATE SOLUTIONS

The Ohio State University
Ph.D. 1984

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ENVIRONMENTALLY-CONTROLLED CRACK GROWTH RATE OF
TYPE 304 STAINLESS STEEL IN HIGH
TEMPERATURE SULFATE SOLUTIONS

DISSERTATION

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

By
Paul Chi-keung Chung, B.A., M.S.

* * * *

The Ohio State University
1984

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Adviser
Department of Metallurgical Engineering
DEDICATION

To my Mom and Dad,
and my wife, Gloria
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CHAPTER I
INTRODUCTION

The intergranular stress corrosion cracking (IGSCC) of sensitized Type 304 stainless steel in high temperature (100-290 °C) aqueous environments, particularly high purity water containing dissolved oxygen, has been extensively investigated during the last decade [1-5], as a consequence of cracking incidents in boiling water reactors (BWRs). While these incidents have not constituted a hazard or safety issue to the public [6], they have cost utility companies enormous amounts of money for replacement power and repairs. It has been estimated that the loss of 1000 MW of nuclear power during an outage would cost one million dollars a day [2,7]. Furthermore, a painful decision was recently made by Nine Mile Point BWR to replace the cracked primary piping system at an estimated cost of $150 million [8].

It is well known that the elements necessary for IGSCC are a critical level of stress, a sensitized microstructure, and specific environmental conditions. The environmental conditions for IGSCC are fulfilled when the corrosion potential of the Type 304 stainless steel lies above a certain critical corrosion potential. The dissolved oxygen,
generated by the radiolysis of water, at the normal BWR operating condition, is sufficient to increase the corrosion potential above the critical potential for IGSCC. The sensitized microstructure is produced by chromium depletion along grain boundaries within the heat affected zone (HAZ) formed during welding due to the precipitation of chromium carbide. The stresses responsible for the SCC are believed to be primarily residual welding stresses, but the contribution of tensile and vibrational stresses during start-up and on-load operation can also be significant.

In most of the laboratory studies carried out during recent years [4, 9-15], strain rate tests have been employed to determine the susceptibility of Type 304 stainless steel to IGSCC. The advantage of this technique is that cracks can be initiated more rapidly than in conventional constant load tests. Consequently, the effect of environmental variables, as well as the influence of the degree of sensitization (DOS), on the cracking behavior, including crack growth rate, crack mechanism, and critical potential for crack propagation, can be more easily evaluated. However, an active interest exists in measuring crack growth rates using fracture mechanics techniques.

It is believed that a knowledge of the rate of IGSCC can affect the design and operation of nuclear reactors in several ways [16]. Critical flaw sizes are set to ensure that the leak-before-break criterion is obeyed and to
assess the available margin of safety. Crack growth rates also play a role in the selection of inspection intervals and the determination of piping lifetimes. To predict the life of stainless steel pipe welds that are subject to failure from IGSCC, it is important to establish appropriate initial flaw size acceptance criteria and to measure accurately the rate of growth of cracks.

The current research study was carried out for the following purposes:

1. To measure crack growth rates for sensitized Type 304 stainless steel in high temperature dilute aqueous solutions at various applied potentials by using modified wedge-opening-loading (WOL) specimens loaded under the constant deflection condition.

2. To develop an inexpensive loading device that will allow the measurement of the relaxation of the load as the crack extends under the influence of the environment in high pressure/high temperature systems.

The advantage of this technique (specimen geometry and loading conditions) arises from the fact that the crack length, the crack growth rate, and $K_I$ can be calculated at any given time from the compliance curve for the specimen. In principle, a complete $da/dt \approx f(K_I)$ curve can be obtained using a single specimen [17], particularly over the $K_I$ range that is important in pipe cracking ($K_I \ll K_{IC}$).
This dissertation is divided into four main sections. The literature survey provides the necessary background information. The section entitled "Experimental Details" describes the materials, experimental apparatus, and experimental procedures used in the course of the investigation. The results and analysis are included in the third main section and a discussion of the results follows in the fourth section.
CHAPTER 2
LITERATURE SURVEY

2.1 IGSCC IN BWR PIPING

2.1.1.1 Boiling Water Reactor

The direct cycle boiling water reactor (BWR) nuclear system (Figure 2-1) is a steam-cycle conversion system [18]. It produces steam in the reactor core as in a fossil-fueled boiler, and the generated steam drives a conventional turbine generator to produce electricity in a similar manner to that in fossil-fueled power plants. However, nuclear radiation from the nuclear core, as well as from the generated steam, requires in the nuclear power plants a much higher safety standard than that of traditional power plants. Therefore, the capital investment, the difficulties in design and construction, and the complexity in the operation and management of a BWR nuclear system are several degrees higher than those of regular power plants.

In general, a BWR (Figure 2-2) consists of a nuclear core and an internal structure assembled within a pressure vessel, auxiliary systems to accommodate the operational and safeguard requirements of the nuclear reactor, and necessary controls and instrumentation [19]. Under normal operating conditions, the steam and water mixture, generated in the reactor core, passes through steam/water separators to remove the water. Then a relatively dry steam (99.9%) is
Figure 2-1. Simplified schematic of boiling water reactor [18].
Figure 2-2. Schematic of water/steam circulation system of boiling water reactor [19].
produced by the steam dryers. The dry steam, at approximately 1000 psi (7 MPa) and 550 °F (288 °C), enters the main steam lines, and is directed to the steam turbine-generator. Finally, the turbine employs a conventional regenerative cycle with condenser deaeration and condensate demineralization.

The primary materials of construction for the major components of a typical BWR are listed in Table 2-1 [18]. Type 304 stainless steel is widely used for components such as piping, valves, pumps, and condenser tubes.

2.1.2 The Primary BWR Environment

The primary BWR environment is high purity water (conductivity < 0.1 micro simens/cm, Cl<sup>-</sup> < 0.2 ppm) [20,21]. Generally, the water circulating through the reactor cycle can be characterized in two ways. The first is by determining the combinations of temperature and chemical species that occur. The second is by the combinations of temperature and electrochemical potentials (ECP) that occur [20].

While the BWR is operating under normal conditions, the water is maintained at a high purity level. The primary chemical species are limited to dissolved gases. Radiolysis of water in the reactor core produces oxygen, hydrogen, and hydrogen peroxide [20]. The temperature-oxygen combinations, temperature-hydrogen combinations, and temperature-hydrogen peroxide combination that have been measured in BWRs are presented in Figure 2-3(a), (b) and, (c), respec-
Table 2-1

Major Components and Materials in Nuclear Systems

<table>
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<tr>
<th>Reactor component</th>
<th>BWR</th>
<th>PWR</th>
<th>LMFBBR</th>
<th>Tokamak</th>
<th>Inertial confinement</th>
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<td>Fuel assembly</td>
<td>(\text{UO}_2)/Zircaloy 2, 4</td>
<td>(\text{UO}_2)/Zircaloy 4</td>
<td>(\text{UO}_2), 25 ± 5% (\text{PuO}_2)/Type 316 SS*</td>
<td>D-T</td>
<td>D-T</td>
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<td>Control materials</td>
<td>(\text{B}_4\text{C}/\text{Type 304 SS})</td>
<td>(\text{Ag}-\text{Cd alloy})</td>
<td>(\text{B}_4\text{C}/\text{Type 316 SS})</td>
<td>NA*</td>
<td>NA</td>
</tr>
<tr>
<td>Breeding blanket</td>
<td>NA</td>
<td>NA</td>
<td>(\text{UO}_2)/Type 316 SS</td>
<td>NA</td>
<td>Li/Li-containing material</td>
</tr>
<tr>
<td>Reactor Vessel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell</td>
<td>Low-alloy steel (SA533 Gr. B)</td>
<td>Low-alloy steel (SA533 Gr. B, SA508)</td>
<td>Type 304 SS</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Cladding</td>
<td>Type 304L SS (SA364*)</td>
<td>Type 304 SS; Inconel 617</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>First wall/blanket</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>Type 304, 316, 347 SS; 9-12Cr, 1-2Mo steels</td>
<td>Assume same as LMFBBR</td>
</tr>
<tr>
<td>Steam generator</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell</td>
<td>Low-alloy steel (SA533 Gr. B)</td>
<td>Type 304 SS or 316 SS</td>
<td>21Cr-1Mo steel (SA 350)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Support plates</td>
<td>NA</td>
<td>NA</td>
<td>Carbon steel (SA515 Gr. 60)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Piping</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Valves</td>
<td>Type 304 SS or 316 SS; 9CR or 12Mo steels (SA105, 316, 9Cr-1Mo-1V or SS 321)</td>
<td>Type 304 SS or 316 SS</td>
<td>Type 304 or 316 SS</td>
<td>21Cr-1Mo steel or Type 304, 316 SS</td>
<td>21Cr-1Mo steel or Type 304, 316 SS</td>
</tr>
<tr>
<td>Pumps</td>
<td>Type 304 SS (SA316); 9Cr-1Mo steel</td>
<td>Type 304 SS; Stellite</td>
<td>Type 304 SS or 21Cr-1Mo steel</td>
<td>Type 304 SS or 316 SS</td>
<td></td>
</tr>
<tr>
<td>Condenser</td>
<td>Al-Bronze; Al-brass (SB261); Cupronickel (SB111, 251); Titanium (SB338); Type 304 SS (SA249)</td>
<td>Al-Bronze; Al-brass; Cupronickel; Titanium: Type 304 SS</td>
<td>Titanium</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Turbine Generator</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rotor</td>
<td>Cr-Mo-V or Al-Ni-Mo steels (A400, 470, 471; Type 403 SS; Ti-6Al-4V)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Disc</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blade</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* SS = stainless steel.
* NA = not applicable.
* Candidate materials.
Figure 2-3. Variation of a) Oxygen, b) Hydrogen, c) Hydrogen Peroxide, and d) Electrochemical potential with temperature during startups and steady states of several BWR systems [20].
tively. It is noted that, during the start-up period, with the temperature below 200 °C, all the gases vary widely. No specific pattern can be followed. However, at the steady-state operating condition (288 °C), the oxygen is between 30 and 350 ppb, the hydrogen is between 15 and 30 ppb, and the hydrogen peroxide is zero due to its decomposition above 170 °C.

The combinations of temperature and ECP that occur in the BWRs are summarized in Figure 2-3(d). The value of ECP is approximately 200 to 500 mV\textsubscript{SHE} at the start-up, and gradually decreases to about 0 to -300 mV\textsubscript{SHE}. Basically, the ECP is a measurement that accounts for all the chemical species present in the solution. However, the ECP measured in a BWR cannot be directly related to the concentration of the dissolved species. This is because the electrochemical systems may not achieve thermodynamic equilibrium [20,21].

2.1.3 **History of IGSCC in BWR Piping Systems**

The IGSCC of the BWR piping, nozzles, and safe ends (Figure 2-4) [22] has been a subject of concern since 1965, when furnace-sensitized stainless steel components cracked in the Dresden-1 reactor [23]. However, beginning in 1974, the generic nature of the problem was recognized as being the result of a wide-spread outbreak of cracks in 4-inch diameter (10.2 cm) bypasses (see Figure 2-5), and 10-inch diameter (25.4 cm) core spray pipings [24,25]. In 1978, the first instance of cracking in a 24-inch diameter (61 cm)
Figure 2-4. Incidences and locations of stress corrosion cracking in BWR pressure boundary [22].
Figure 2-5. A detailed schematic of a typical recirculation loop arrangement [27].
line was reported at the Gundremmingen ("KRB") Unit in Germany, and extensive full-circumferential cracking occurred in all eight inlet nozzle safe ends on the Duane Arnold BWR [26]. Most recently (in 1982), a large number of cracks was discovered in the 28-inch diameter (71 cm) primary recirculation lines at the Nine Mile Point BWR. Subsequently, cracking was detected in large diameter Type 304 stainless steel lines in Monticello, Hatch Unit 1, Browns Ferry Unit 1 and Dresden Unit 2 [8]. The frequency of cracking as a function of pipe diameter for world-wide boiling water reactors is shown in Figure 2-6 [27]. It is now clear that no welded Type 304 stainless steel component in a BWR can be considered immune from the threat of IGSCC.

In spite of the 380 incidents, there has never been a reported case of pipe severance. Pipe cracking incidents do not constitute a safety issue, and the industry and Nuclear Regulatory Commission (NRC) position is the "leak-before-break" concept. A leak will occur before the tough ductile austenitic stainless steel pipe will experience a complete separation [27]. However, pipe cracking has created serious problems of plant availability and economics to the utility industry. In addition, radiation exposure of skilled personnel and of expensive equipment involved in inspection and repair operations is of concern to the utilities.
Figure 2-6. The frequency of IGSCC incidents as a function of pipe diameter [27].
2.2 Fundamental Understanding of Stress Corrosion Cracking

The first time that stress corrosion cracking (SCC) caught the attention of engineers was in the second half of the 19th century when an accident took place in a cold-drawn brass tube used in the electric power industry [28]. Since then, stress corrosion cracks have been reported for other alloys, such as aluminum alloys (1920), austenitic steel (1930), magnesium alloys (1950-1960), and zirconium alloys (1970).

Basically, SCC is a process associated with a combination of tensile stress (applied or residual), environment, and microstructural features (Figure 2-7) which lead to component failure due to the initiation and propagation of a high aspect ratio crack, as shown in Figure 2-8 [29]. If any one of these necessary conditions is removed, cracking may cease.

Advances in the mechanistic understanding of SCC could briefly be classified into three stages [29]. In the first stage, 1940 to 1965, the problem was identified and categorized in terms of specific alloy/aggressive couples (Table 2-2) [30]. The second stage was a mechanistic analysis stage, between 1965 and 1975, in which various mechanisms were proposed to explain the crack morphology, the dependency of cracking on various electrochemical and metallurgical parameters, and the wide range of crack propagation
Figure 2-7. Venn diagram indicating the need for stress, environment, and microstructural requirements in stress corrosion cracking.
Figure 2-8. The sequence of events which could occur in stress corrosion cracking testing of a smooth specimen [29].
Table 2-2

Recognized Stress Corrosion System Between 1960 and 1965

<table>
<thead>
<tr>
<th>Material Class</th>
<th>Corrosion Systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mild-Steel</td>
<td>( \text{OH}^-, \text{NO}_3^-, \text{NH}_4^+, \text{CO}_2/\text{CO}_3^{2-}/\text{HCO}_3^- )</td>
</tr>
<tr>
<td>Low Alloy Ferritic Steel</td>
<td>( \text{Cl}^-, \text{OH}^-, \text{H}_2\text{O}(\text{O}_2) )</td>
</tr>
<tr>
<td>( \gamma ) Stainless Steel</td>
<td>( \text{Cl}^- )</td>
</tr>
<tr>
<td>Aluminum Alloys</td>
<td>( \text{NH}_4^+ )</td>
</tr>
<tr>
<td>Copper Alloys</td>
<td>( \text{H}_2\text{O}, \text{H}_2(\text{g}), \text{H}_2\text{S}(\text{g}) )</td>
</tr>
<tr>
<td>High-Strength Steels</td>
<td>( \text{Cl}^-, \text{NO}_3^-, \text{Fused Salts, CH}_3\text{OH} )</td>
</tr>
<tr>
<td>Titanium Alloys</td>
<td></td>
</tr>
</tbody>
</table>
rates observed. This information has been documented in the proceedings of a series of conferences [31-41]. Finally, in the present stage, engineers are starting to apply the mechanistic knowledge to practical needs. These needs include improving the predictive capabilities of the cracking mechanism, developing testing techniques which are relevant to practice, giving guidelines to the development of material or environmental control, and identifying potential damage for the actual alloy/environment system [30].

2.2.1 The Models and Mechanisms of SCC

The models describing SCC divide into two major groups [42]: anodic dissolution [43-46], and mechanical fracture [43,44], see Table 2-3. Among them, the slip-dissolution model [45,46], modified by Staehle from the film-rupture model [43,44], is the most accepted one for describing the SCC phenomenon, especially for ductile material. The film-rupture model was originated by Champion and Logan [43,44]. The basic assumption is that a protective surface film at the crack tip is ruptured by localized plastic deformation, permitting a rapid dissolution of the exposed substrate while the non-deforming crack walls remain protected by the film (Figure 2-9(a)). Later, Staehle [45,46] adopted a more atomically-related view of this model. They suggested that the film rupture is a result of the emergence of slip steps through the passive film (Figure 2-9(b)).
Table 2-3
Proposed Models for Propagation of SCC

**DISSOLUTION MODEL**

Film-rupture model. The essential feature of this model is that protective surface film is ruptured by localized plastic deformation at the crack tip, permitting propagation by anodic dissolution of the exposed metal.

**MECHANICAL FRACTURE MODELS**

Model based on ductile fracture:

Tunnel model. This model is based on the observations of fine corrosion tunnels in certain stress-corrosion systems. Crack extension is considered to occur discontinuously by the ductile tearing of ligaments between parallel tunnels.

Models based on brittle fracture:

1. Absorption model. It is postulated that specific ions adsorb and interact with strained bonds at the surface of the metal at the crack tip, reducing the bond strength and permitting continuous brittle fracture at low stresses.

2. Bulk-embrittlement models,

   (i) Hydrogen embrittlement. Several mechanisms have been proposed, including models involving the formation of brittle, stress-induced hydrides, and decohesion (similar to the adsorption model but in which embrittlement is considered to occur in the lattice).

   (ii) Selective dissolution. This has been suggested as a means of triggering discontinuous cleavage in the resulting porous zone.

   (iii) Tarnish rupture. Specifically proposed for the brass-aqueous NH₃ system but applicable to any system in which thick films are produced, this model proposes that cracking is confined to a brittle phase which grows into the metal ahead of the crack front.
Figure 2-9. Schematic drawing of a) Film-rupture model [43], and b) Slip dissolution model [45].
Parkins further classified the mechanisms of stress corrosion cracking into three broad categories [49]: pre-existing active path mechanisms [50-52], strain-assisted active path mechanisms [53-60], and adsorption-related phenomena [61, 62]. For interpreting the intergranular cracking of ductile alloys in aqueous environments, pre-existing active path mechanisms have been applied by Ford [30] and many other authors [50-52]. They related the cracking susceptibility to the chemical activity of the grain boundary. This meant that a localized intergranular attack was due to one of the following reasons: a) the existence of an inherently higher activity of the disordered grain boundary structure, b) the presence of chemically active grain boundary impurities, namely precipitates, or c) the occurrence of the solute-depleted zone adjacent to the precipitate.

As suggested by Kawakubo and co-workers [63], the combination of the slip-dissolution model and the pre-existing active path mechanisms mentioned above is the most accepted mechanistic model to describe the IGSCC process in sensitized austenitic stainless steel in a BWR environment of oxygenated high temperature pure water. As illustrated in Figure 2-10 [63], along the active path (Cr-depleted zone), the IGSCC propagates through the repetition of the following three steps: (1) Fracture of protective films on the metal surface due to straining, (2) anodic dissolution of the
Figure 2-10. Schematic drawing of SCC along grain boundaries [63].
bared Cr-depleted zone, and (3) repassivation.

2.2.2 The Crack Growth Response of SCC

For many systems [28, 29, 34, 64], the crack propagation rate, \( V \), has a characteristic relationship with the applied stress intensity factor, \( K \), as shown in Figure 2-11 [28]. The curve can be divided into three regions. The crack propagation does not occur at a discernible rate below \( K_{ISC} \), but rises rapidly with stress intensity in the Stage I region. At higher stress intensities in the Stage II region, the \( dV/dk \) value decreases and may become zero. The rate determining step is suggested to be due to mass transfer and diffusion processes. The third region generally occurs at stress intensities close to \( K_{IC} \), where the crack growth rate again becomes dependent upon stress intensity.

According to the slip-dissolution model, the SCC processes include three major types of reactions, namely, passivation [65-74], liquid diffusion [75], and oxide rupture [76-79]. Advances in the mechanistic understanding of the crack growth rate have been associated with quantitatively defining these rate determining reactions and their relationships in Stage I and Stage II crack propagation. As suggested by Ford [80], the change in the crack propagation rate with various fundamental controlling parameters can be represented by a reaction surface (Figure 2-12) [80]. The crack propagation process can be interpreted by the response
Figure 2-11. Schematic representation of crack growth rate versus stress intensity relationship [28].
Figure 2-12. Reaction surface illustrating the variation in crack propagation rate by the slip-dissolution model with changes in passivation rate, oxide rupture rate, and liquid diffusion rate [80].
on this reaction surface for a specific alloy/environment system [80].

The work of Ford [80, 81] indicates that a sensitized stainless steel/dilute aqueous environment system at 98 °C is an example of a strongly passivating system, as shown in Figure 2-13 [80]. The crack response curve follows path (a) in Figure 2-12. One obvious remedy to reduce the SCC in this system is to increase the oxygen content in the solution in order to increase the passivation rate of the alloy [80].

On the other hand, based on some preliminary data, Ford theoretically predicted that the oxide rupture was the rate determining step of sensitized Type 304 stainless steel in \( \text{H}_2\text{O}/0.2 \text{ ppm O}_2 \) at 288 °C. The crack response curve should follow path (c) in Figure 2-12. Since the film rupture rate is mainly controlled by the strain rate at the crack tip, the crack growth rate should also be governed by the strain rate, shown in Figure 2-14 [80]. Furthermore, by rearranging data from various sources (see Figure 2-15(a)), Ford [80] also predicted that the \( K_{\text{ISCC}} \) value for fracture mechanics specimens should change with the degree of plastic constraint at the crack tip (Figure 2-15(b)). Ford's approach is a very good example of using the mechanistic knowledge to predict practical problems. However, there are too many uncertain assumptions in his theoretical predication, and the reliability of the preliminary data he adopted
Figure 2-13. Variation in oxidation rate with time from creation of bared surface on Fe12Cr10Ni and Fe18Cr8Ni in 0.01 M Na₂SO₄, 98 °C at 193 mV SHE. (Noted up to 1 sec. after creation of the bared surface the passivation rate on the alloy simulating Cr-depleted zone is markedly slower than at the grain matrix.) [80].
Figure 2-14. Comparison between observed and theoretical crack propagation rate/strain rate relationship for furnace sensitized Type 304 stainless steel in water/0.2 ppm oxygen at 288 °C [80].
Figure 2-15 a) Crack propagation rate/stress intensity relationships for sensitized Type 304 stainless steel in water/8 ppm oxygen at 288°C. b) Variations of $K_{ISCC}$ with $B/W$ ratio derived from Figure a) [80].
is doubtful. More experimental work should be done to verify his argument.

Finally, if the crack propagation rate is increased to a critical value, a further increase in the crack propagation rate becomes controlled by the liquid diffusion of either solvating ligands to the crack tip or solvated metal cations away from the crack tip. The liquid diffusion rate may be affected by either solution flow rate or by mechanically related solution renewal effects of cyclic loading. In this case, the crack propagation rate should follow path (d) on the reaction surface in Figure 2-12.

A suggested variation in the environment-controlled crack propagation rate with stress intensity for the major factors mentioned above is summarized in Figure 2-16 [80]. The crack growth rate in Stage I and Stage II is not only governed by a single rate determining step, but also the crack tip deformation rate (COD) plays an important role in affecting both the minimum theoretical $K_{ISCC}$ and the maximum theoretical crack velocity ($da/dt$). This fact implies that design criteria should not be based on data obtained from a single type of statically loaded specimens. More data are required for specimens tested under different loading conditions to obtain a better understanding of these interrelated steps.
Figure 2-16. Suggested variation in environment-controlled crack propagation rate with stress intensity for different rate determining steps [80].
2.3 Primary Contributing Factors to IGSCC of Sensitized Type 304 Stainless Steel in BWR Piping

2.3.1 Sensitized Microstructure

2.3.1.1 Fundamental Understanding

The phenomenon of sensitization has been reviewed extensively by the present author [82, 83] and others [84, 87] and will not be described in detail here. Briefly, an alloy is said to be "sensitized" if it is more susceptible to IGSCC than a non-sensitized sample of the same alloy. This sensitized condition for Type 304 stainless steel is usually the result of isothermal exposure to temperatures between 550 and 800 °C. The almost universally accepted explanation for sensitization is the chromium depletion theory of Bain, Aborn, and Rutherford [88], which attributes the increased susceptibility to the formation of chromium rich carbide \( M_{23}C_6 \), where \( M = (Cr_{1-x})(Fe,Ni)_x \) and \( x \) is in the range of 0.2 to 0.3] particles along grain boundaries, and the accompanying depletion of chromium from a highly localized zone, about 300 to 5000 Å in width, near grain boundaries [89].

The most common cause of sensitization, especially in the nuclear reactor industry, is encountered by welding. For instance, there are about 6000 welds in the piping systems alone of a modern BWR [90]. During a welding process, the base alloy experiences an intensive localized heat flux which melts the matrix locally. Upon cooling to room temperature, different sections of the base metal will
experience different heat treatments. Figure 2-17 [91] shows the structural changes and the possible problems which may result in various sections of a welded material. Generally speaking, as in Figure 2-18 [89], the carbides are most likely to nucleate at the HAZ, about 0.5 cm from the weld center line, during simultaneous thermal and strain transients that occur during the multiple weld passes used to make a normal pipe butt weld. In some instances prior partial sensitization is found in as-received pipe, due to improper mill practice, and this aggravates pipe weld crack susceptibility. The sensitized HAZ usually extends for only about 0.2 to 0.5 cm on either side of the weld fusion line for typical Schedule 80 Type 304 stainless steel pipe. Solomon's study further indicated that the superposition of the multiple temperature-time pulses from the passing weld bead on the weld shrinkage deformation enhances the kinetics and induces carbide nucleation and growth at a faster rate than otherwise anticipated rate [92, 99, 98].

2.3.1.2 Low Temperature Sensitization

In most cases, the degree of sensitization (DOS) that occurs upon welding is not severe. However, it has been shown by Povich (76-78) that increased sensitization can subsequently develop at temperatures well below the normal sensitization temperature range if carbide nuclei are present. The phenomenon has been referred to as low temperature sensitization (LTS).
<table>
<thead>
<tr>
<th>Heat Affected Zone</th>
<th>Solution Anneal Zone</th>
<th>High Temperature Zone</th>
<th>Weld Metal Zone</th>
<th>Fusion Zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>structural changes:</td>
<td>structural changes:</td>
<td>structural changes:</td>
<td>structural changes:</td>
<td>grain boundary</td>
</tr>
<tr>
<td>Chromium Carbides precipitate</td>
<td>Chromium Carbides dissolve</td>
<td>Chromium Carbides dissolve</td>
<td>Niobium Carbides dissolve</td>
<td></td>
</tr>
<tr>
<td>Chromium Nitrides precipitate</td>
<td>Chromium Nitrides dissolve</td>
<td>Chromium Nitrides dissolve</td>
<td>Titanium Carbides dissolve</td>
<td></td>
</tr>
<tr>
<td>possible problems:</td>
<td>possible problems:</td>
<td>possible problems:</td>
<td></td>
<td>liquidation</td>
</tr>
<tr>
<td>intergranular corrosion</td>
<td>knife line attack</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>intergranular stress corrosion cracking</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>550-800 C</td>
<td>800-1250 C</td>
<td>1250-1350 C</td>
<td>1000-1450 F</td>
<td>1450-2250 F</td>
</tr>
</tbody>
</table>

Figure 2-17. Possible mechanisms for disintegration of welded austenitic stainless steel [91].
Figure 2-18. Grain boundary area fraction covered with carbides for as-welded and LTS conditions, and mass of chromium depletion from grain boundary versus distance from weld centerline for Type 304 stainless steel pipe weldments [89].
From a thermodynamic point of view, carbides could grow at a temperature below the critical temperature range [96, 97] but their growth rate is limited by the diffusion rate of chromium below that critical range. However, the physical changes that occur upon welding, such as increased dislocation density, are suspected to enhance subsequent diffusion processes [98, 99]. The study of Povich and Rao [94] indicates that the rate of LTS obeys an Arrhenius temperature dependence. This dependence corresponds to an activation energy for chromium diffusion of the order of 170 KJ per mole which is only half the expected value for the bulk diffusion of chromium. Based on this diffusion rate, an empirical estimate by Povich and Rao is that an LTS enhanced susceptibility to IGSCC might occur in 10-20 years in the weld HAZ of Type 304 stainless steel (Figure 2-19). The experimental TEM and analytical studies by Rao also revealed an increased width of the depleted chromium profile with LTS treatments as shown in the schematic drawing in Figure 2-20 [92].

Extensive studies on this topic have been carried out by many researchers [16, 100-102]. According to their observations, the deterioration effects of LTS were not as bad as the prediction of Povich and Rao [94]. The crack initiation study of Andresen [102] in oxygenated pure water by using the CERT test technique indicated that the initiation of cracking in oxygenated, high purity water at 200 °C
Figure 2-19. Low temperature sensitization Time-Temperature dependence of IGSCC. The number inside each circle is the strain to failure in CERT at 288 °C. The straight line was drawn so that the strain to failure for points above the line was greater than 18%, representing severe IGSCC [94].
Figure 2-20. Schematic chromium and carbon profiles from carbide grain boundary region into bulk of sensitized Type 304 stainless steel for as-welded and as-welded plus LTS conditions [92].
or 288 °C is more sensitive to the furnace sensitized specimen than to the specimen which was as-welded plus LTS. Therefore, he suggested that the initiation of cracking in that environment is more sensitive to the width of the chromium depleted region than to the depth of the concentration trough. Furthermore, if the depletion trough becomes too narrow as a region, it may not be fully "visible" to the test environment [101, 102].

The work of Schmidt, Caligiuri, and Lawrence [16] using compact tension specimens prepared from a welded pipe, further indicated that, for the simulated BWR start-up and steady state environments (180 °C/1 ppm O₂ and 288 °C/0.2 ppm O₂, respectively), high crack growth rates (about 10⁻¹⁰ m/s at K₁ range between 20 and 30 MPa m¹/²) were obtained from weld HAZ with LTS heat treatments at 500 or 400 °C (Figure 2-21). However, in the same environments, no IGSCC was observed from LTS heat treatments at 360 °C (more than 3000 hours) and below. Therefore, a bi-linear Arrhenius analysis was used by these researchers to describe the LTS heat treatment time and the temperature dependence of the susceptibility to IGSCC (Figure 2-22). The position of the break suggests that two sequential processes determine the IGSCC susceptibility. Activation energies obtained from the trend lines, 86 kJ/mole and 420 kJ/mole for the low and high temperature regions, respectively, are not comparable to the chromium dislocation core diffusion (170 kJ/mole) or
Figure 2-21. Constant load crack growth rate data for LTS heat treated Type 304 stainless steel weld HAZ. Test environment was in elevated high purity water with dissolved oxygen [16].
Figure 2-22. Low temperature sensitization Time-Temperature dependence of IGSCC [16].
the chromium matrix diffusion (280 kJ/mole) in stainless steel. According to this figure, it would take more than 40 years to obtain the LTS enhanced susceptibility to the IGSCC at the BWR operating temperature for the welded stainless steel piping.

However, the results mentioned above are not enough to reach a conclusion on safety in the LTS stainless steel piping. The study of Wei, Novak and Williams [103] indicated that the constant load compact specimen (an increasing K type specimen) is not suitable for studying $K_{ISCC}$ and the crack growth rate for materials with a long initiation time. They observed, that by increasing the cut-off time from 100 hours to 10,000 hours, the apparent $K_{ISCC}$ of constant load cantilever bend specimens, made of high alloy steel (180 ksi y.s.) in synthetic sea water, decreased from 170 ksi in$^{1/2}$ to 25 ksi in$^{1/2}$. Thus, the fact that no IGSCC was detected by Schmidt and co-worker [16] for specimens sensitized below 360 °C may be because the cut-off time of their experiment was not long enough. Furthermore, since it already takes a long period of time, about ten to twenty years, for the HAZ to increase to a critical DOS to promote the IGSCC at the BWR operating environments, the initiation time after the HAZ reaches the critical DOS may not be as long as expected when based on the laboratory study. Therefore, more carefully designed research is necessary to identify the affect of the LTS on the service life of the BWR pipings. For
example, as suggested by Wei and co-workers, a constant displacement (decreasing K) specimen may yield a more reliable result in determining the $K_{ISCC}$ and the crack growth rate for specimens with a long initiation time.

2.3.1.3 Effect of the Degree of Sensitization

In the laboratory, the specimens used to study the effect of DOS were furnace sensitized, by heating in a furnace at a constant temperature within the critical temperature range for a certain period of time. It has been found [1, 3, 89, 91] that the IGSCC susceptibility of Type 304 stainless steel increases with increasing DOS before the steel is over-aged or called "over-sensitized". For example, as found by Clarke and Gordon [104] an increase in the time of sensitization from 5 to 15 hours at 593 °C decreased significantly the average time of the failure of the specimens tested at 288 °C/100 ppm oxygen under an applied stress of 49.5 ksi (341.3 MPa), (Figure 2-23). On the other hand, no significant difference in the time of the failure was observed for specimens treated for 16 or 24 hours at 593 °C. These results are in partial agreement with those of Berry et al. [105], who did not find any marked difference between the behavior of specimens heated for either 7 or 24 hours at 621 °C when tested under constant load conditions at 288 °C in pure water containing 1000 ppm oxygen.
Figure 2-23. Effect of sensitization treatment on the IGSCC of Type 304 stainless steel tested in 288 °C water containing 100 ppm of dissolved oxygen at an applied stress of 49.5 ksi [104].
Using the slow strain rate technique, Hishida and Nakada [11] further found a significant difference between the elongation-to-fracture of the specimens treated for 0.5 and 2 hours at 650 °C. No significant difference was found between the elongation-to-fracture of the specimens treated for 2 and 24 hours. Figure 2-24 shows the results of these tests carried out in air-saturated water at 290 °C using a strain rate of $5 \times 10^{-4}$ per minute. The solution-annealed sample was tested in water and showed almost the same elongation-to-fracture as the specimens tested in air. No IGSCC was observed. Similar results have also been reported by Takaku et al [106].

2.3.1.4 Method for Evaluating DOS

Recognizing the importance of the DOS, attempts have been undertaken to quantitatively correlate the susceptibility of stainless steel to IGSCC in high purity water. The results were obtained by using different standard test methods for intergranular corrosion recommended by ASTM, as seen in Table 2-4 [85, 107]. The outcome of these attempts led to the development of several electrochemical methods for measuring the DOS, which include the electrochemical potentiokinetic reactivation (EPR) method [108], the anodic polarization curve technique [83, 109] and the constant potential etching technique [83, 109]. There are several publications [85, 110, 111] in which different methods for measuring the DOS of stainless steels have been compared,
Figure 2-24. Stress-elongation curves for sensitized Type 304 stainless steel strained at $5 \times 10^{-4}$/min in air-saturated pure water at 290 °C [11].
Table 2-4 Summary of Chemical Tests used for the Determination of Susceptibility to Intergranular Corrosion of Iron—Nickel—Chromium Alloys

<table>
<thead>
<tr>
<th>Test Name</th>
<th>Reference</th>
<th>Usual Solution Composition</th>
<th>Test Procedure</th>
<th>Quantitative Measure</th>
<th>Potential Range, Volts (Standard Hydrogen Scale)</th>
<th>Species Selectively Attacked</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Nitric Acid Test</td>
<td>1</td>
<td>65 wt % HNO₃</td>
<td>Five 48-h exposures to boiling solution. Solution refreshed each period</td>
<td>Average weight loss per unit area of five testing periods</td>
<td>+ 0.99 to + 1.20</td>
<td>1. Chromium—depleted areas</td>
</tr>
<tr>
<td>2. Acid Ferric Sulfate Test</td>
<td>1,4</td>
<td>50 wt % / H₂SO₄ + 25 gm/l Ferric sulfate</td>
<td>120-h exposure to boiling solution</td>
<td>Weight loss per unit area</td>
<td></td>
<td>2. Sigma phase</td>
</tr>
<tr>
<td>3. Acid Copper Sulfate Test</td>
<td>1–2</td>
<td>16 wt % H₂SO₄ + 100 grams/l CuSO₄ (+ metallic copper)</td>
<td>72-h exposure to boiling solution</td>
<td>1. Appearance of sample upon bending</td>
<td>+ 0.30 to 0.58</td>
<td>3. Chromium carbide</td>
</tr>
<tr>
<td>4. Oxalic Acid Etch</td>
<td>1</td>
<td>100 gm H₂C₂O₄·2H₂O + 900 ml H₂O</td>
<td>Anodically etched at 1 A/cm² for 1.5 min</td>
<td>1. Geometry of attack on polished surface at 250X or 500X</td>
<td>+ 1.70 to + 2.00 or greater</td>
<td>1. Various carbides</td>
</tr>
<tr>
<td>5. Nitric – Hydrofluoric Acid Test</td>
<td>1</td>
<td>10% HNO₃ + 3% HF</td>
<td>4-h exposure to 70°C solution</td>
<td>1. Comparison of ratio of weight loss of laboratory annealed and as-received samples of same material</td>
<td>a. Corrosion potential = 304 – 0.14 to +0.54</td>
<td>1. Chromium—depleted areas, 2. Not for sigma phase, 3. Used only for Mo bearing steels</td>
</tr>
<tr>
<td>6. Hydrochloric Acid Test</td>
<td>3</td>
<td>10% HCl</td>
<td>24-h in boiling solution</td>
<td>1. Appearance of sample after bending around mandril</td>
<td>a. Redox potential = +0.32</td>
<td>1. Alloy depleted area</td>
</tr>
<tr>
<td>7. Nitric Acid – Cr⁶⁺ Test</td>
<td>5</td>
<td>5W H₂SO₄ + 0.5W K₂Cr₂O₇</td>
<td>Boiling with solution renewed every 2 to 4 h for up to 100 h</td>
<td>1. Weight loss per unit area</td>
<td>a. Redox potential = +1.37</td>
<td>1. Solute segregation to grain boundaries</td>
</tr>
</tbody>
</table>
<pre><code>                                                                                                                                                | 2. Electrical resistivity                                            | b. Corrosion potential of 304 = +1.21                               |                                            |
</code></pre>

but it seems that electrochemical methods are the simplest and the most adequate [82, 83, 107, 109]. As concluded by Clarke [112] and Aho-Mantila et al. [113, 114], at present the EPR method seems the most advanced electrochemical method available at present for quantitatively detecting the levels of sensitization that are of interest to the industry.

Basically, the EPR method consists of the measurement of the anodic charge obtained during a reverse potential sweeping in 0.5M H$_2$SO$_4$ + 0.01M KSCN after pre-passivation of the surface. The total charges obtained, $Q$, are further normalized by both specimen size and grain size. Nevertheless, there is still some inconsistency between the results of DOS measurements obtained by the EPR method and the results of SCC susceptibility tests. For example, it was reported [107] that a relatively large grained material with marked susceptibility to IGSCC in oxygenated water at 290 °C was classified by the EPR method as unsensitized. In addition, Ruther et al. [101] observed that the lightly sensitized (700 °C/0.25 hr. + 500 °C/24 hrs., EPR value 2 °C/cm$^2$) Type 304 specimens were found to be more susceptible to IGSCC than the medium sensitized specimens (700 °C/12 hrs., EPR value 20 °C/cm$^2$) at 289 °C pure water/0.05 to 0.2 ppm oxygen under slightly acidic conditions (pH is about 6 at room temperature) in the slow strain rate tests. The lack of agreement between the EPR readings and the IGSCC suscepti-
bility was also observed by Schmidt et al. in their work on the LTS specimen tested in high purity water with dissolved oxygen at elevated temperatures [16].

Therefore, it seems that, as suggested by Szklarska-Smialowska and Cragnolino [3], the potentiostatic etch technique employing 1N HClO₄ + 0.2 N NaCl may serve as a better method than the EPR method for evaluating the DOS of the sensitized Type 304 stainless steel. In this technique, only the continuous Cr-depleted zone near the grain boundaries is revealed [82, 83].

2.3.2 Effect of Stress

The design of the BWR is such that the stresses and strains on structural components are held within limits that ensure macroscopic structural integrity. Since these limits are very conservative, the stresses above the material yield strength would not occur in any part of the structure. However, there are three types of stress in a welded pipe that may contribute to the occurrence of IGSCC in an operating BWR, namely, welding residual stress, dynamic loading, and residual stress produced by grinding [95].

2.3.2.1 Welding Residual Stress

Extensive work has been done by the research group of the General Electric Company in San Jose, California, in measuring welding residual stress around a welded pipe [89].
Their results indicated that residual tensile stresses of over 40 ksi have been measured in the HAZ of the inside surface and sub-surface of welded Type 304 stainless steel piping, shown in Figure 2-25. The combination of this residual stress and the applied stress may result in a total stress state that promotes IGSCC initiation and propagation. On the other hand, less IGSCC susceptibility has been found in some welded pipes which have a compressive type residual stress in the HAZ of the inside surface of the pipe [117, 118]. Usually, the compressive type residual stress of the pipes is produced by newly developed welding techniques (e.g. the heat sink welding process and the last path heat sink welding process) and post-weld heat treatment (induction heating stress improvement). Figure 2-26 [119] shows the effect of induction heating stress improvement of the residual stress distribution on the inner diameter surface of a pipe.

2.3.2.2 Dynamic Loading

In the past, extensive laboratory studies on IGSCC have shown that applied stresses above the yield strength are required for IGSCC to occur in sensitized Type 304 stainless steel in BWR-like environments [95, 120, 122]. However, White and Berry [121, 122] observed IGSCC below the yield strength in high purity water/8ppm dissolved oxygen at 288 °C in a smooth tensile sample of sensitized Type 304 stainless steel that was cyclically loaded. The load was
Figure 2-25. Worst azimuth i.d. residual stress profiles for high heat 4 in., 10 in., and 26 in. Type 304 stainless steel pipe weldments [89].
Figure 2-26. Effect of induction heating stress improvement on the residual stress distribution on the inner diameter surface of a 12 inch Schedule 100 diameter pipe [119].
controlled between 84% and 1% of the yield strength. The loading cycle was approximately 75 minutes at high load, and there were two 5-minute periods of changing load. Failure occurred after 736 cycles and was clearly intergranular. This fracture surface morphology is quite similar to that observed for field conditions [118]. Thus, it appears that dynamic loading during BWR normal operating conditions and start-up contributes to the occurrence of IGSCC at a stress below the yield strength.

2.3.2.3 Surface Grinding

Additional surface residual tensile stress of the order of 100 ksi can be produced by post-weld grinding [118]. Such conditions are observed frequently on the internal diameter surface in the HAZ of a butt welded pipe, as shown in Figure 2-27 [89]. This type of grinding can also introduce severe notch effects and a depth of heavy surface cold work of 100 microns or more. This material often consists of deformation induced martensite. The studies of Wang [124] and Povich [125] each noted that this brittle layer can contribute to the initiation of IGSCC (Figure 2-28) [92]. In addition, subsequent welding operations will introduce localized microstructural changes in that layer, and the resultant transition structure may also provide conditions that increase the susceptibility to IGSCC (Figure 2-27).
Figure 2-27. Schematic of surface structures in welded Type 304 stainless steel as a result of prior machining and grinding operations on the internal surface of the pipe [89].
Figure 2-28. Applied stress-strain behavior of damaged surface skin material versus base pipe material [92].
2.3.2.4 SCC Test in Laboratory

In the laboratory, four types of SCC tests have been developed to study the effect of stress and strain for sensitized, or as-welded, Type 304 stainless steel. They are listed in an increasing order of severity: (1) constant deflection, (2) constant load, (3) slow strain rate, and (4) cyclic loading. All these tests commonly use smooth specimens.

The results obtained by different workers who have employed the first two techniques were reviewed by Cowan and Gordon [1]. They concluded that, at 288 °C in oxygenated pure water, IGSCC was observed only at corresponding stress levels higher than the yield strength of the material at the testing temperature, see Figure 2-29 [104]. In addition, the time it took to failure decreased with increasing stress. Similar results were obtained by Yonezawa and Tsuruta [3] under a constant potential of about 50 mV_SHE in a sodium sulfate solution at 300 °C.

The study of the slow strain rate tensile test was reviewed by Szklarska-Smialowska and Craginolino [3]. In their review, they indicated that a minimum strain is necessary to initiate intergranular cracks. The work of Welch [129] claimed that a 5.5% strain is necessary to initiate the cracks at a constant strain rate of 10^-6/s. In addition, Szklarska-Smialowska and Craginolino [3] also concluded that the crack propagation rate measured in slow strain rate
Figure 2-29. Stress dependency of IGSCC of sensitized Type 304 steel in 288 °C water with 0.2 ppm oxygen [114].
tests depends on the strain rate. For example, as reported by Hishida and Nakada [11], in oxygenated water at 290 °C, the highest strain rate at which IGSCC could be detected was about $9 \times 10^{-5}/s$. If the strain rate is too high, insufficient time is available for the propagation of SCC, and ductile fracture is caused by mechanical overloading. On the other hand, if the strain rate is too low, then either the repassivation rate of the protected film will overcome the bare metal formation rate [153], or the stress will not be high enough to break the film continuously, and crack propagation will be arrested [145, 154].

The cyclic loading test (essentially corrosion fatigue tests) which is the most sensitive technique for detecting SCC has been recently employed in the study of Type 304 stainless steel. For example, White et al. [158] who found IGSCC in a cyclic loading test in 290 °C oxygenated water with a maximum applied stress equal to only 84% of the yield strength, Ford and Silverman [155] and Ford and Emigh [156] also found that, in high purity water at 95 °C, the crack propagation rates were a function of the loading rate and the mean stress, and that the $K_{ISCC}$ would decrease with dynamic loading. More recently, Kawakubo et al. [157] and Tsai [146] further found that either the cyclic frequency or cyclic wave form effected the crack growth rate of sensitized Type 304 stainless steel in an elevated solution environment, as seen in Figure 2-30 [157] and 2-31 [146].
Figure 2-30. Effect of loading frequency on time-based crack propagation rate of Type 304 stainless steel, tested in 290 °C pure water with 8 ppm oxygen [157].
Figure 2-31. Corrosion fatigue crack growth rates in sensitized Type 304 stainless steel as a function of potential and frequency in 0.01m sodium sulfate solutions at K=20 MPa m$^{1/2}$, T=250 °C. Open symbol denotes TGSCC, half-filled symbol denotes mixed of IGSCC and TGSCC, and filled symbol denotes IGSCC [146].
2.3.3 Environment Related Causes

As mentioned previously, the primary BWR environment is high purity water, and the chemical species are limited to dissolved gases. Because IGSCC of Type 304 stainless steel pipe welds occurs in operating BWRs, it is reasonable to conclude that the BWR environment is an environment that will facilitate IGSCC. However, as shown in Figure 2-3, there is no single BWR environment. Instead, there are many BWR environments that are characterized by the oxygen-temperature combination, and the accompanying hydrogen and hydrogen peroxide concentrations. Much research has been done to determine which environments contribute the most to the occurrence of IGSCC.

2.3.3.1 Effect of Oxygen Content and Temperature

The effect of oxygen on the susceptibility of sensitized Type 304 stainless steel to IGSCC in pure water was intensively investigated by many researchers [11, 104, 105, 126-131]. It is now well established that the presence of dissolved oxygen in pure water significantly affects the SCC behavior of sensitized Type 304 stainless steel at both the BWR steady state operating condition and start-up.

The detrimental effect of dissolved oxygen at several temperatures is demonstrated in Figure 2-32 [126]. It shows that the average crack propagation rate increases monotonically with dissolved oxygen concentration, in a range of 0.1 ppm to 32 ppm, under slow strain rate test conditions [126-
Figure 2-32. Estimated crack propagation rate of sensitized Type 304 stainless steel in high temperature water as a function of dissolved oxygen concentration [126].
128, 132]. On the other hand, during constant load tests [104] conducted at oxygen concentrations ranging from 0.2 to about 5ppm, the time-to-failure decreased with increasing concentrations of oxygen, but it appeared to be constant for oxygen concentrations above 5ppm. Combining the efforts of many researchers, EPRI research project No. RP1332-1 [20], summarized the condition, that could facilitate the IGSCC of sensitized Type 304 stainless steel in high purity water (Figure 2-33). The results indicate that the temperature and oxygen combination at the steady state operating condition of BWR, as well as at some part of the start-up condition, is in a region that will facilitate the IGSCC of sensitized stainless steel pipes.

Nevertheless, the beneficial effects in controlling the oxygen content in high purity water have been observed recently by several research groups. The laboratory results of Andresen demonstrate that the oxygen control process (below 0.2 ppm) during start-up improves the life of tested specimens by a factor of 4 to 8 under a variety of different conditions in pure water [133]. Indig and Weber [134] also claim that the IGSCC of severely sensitized Type 304 stainless steel can be eliminated at dissolved oxygen concentrations below 20 ppb in reactor water at 270 to 280 °C. Their results were obtained through the constant extension rate test, and the oxygen content was controlled by hydrogen injection. Owing to the understanding of these facts, con-
Figure 2-33. The shaded region represents combinations of temperature and oxygen that facilitate IGSCC of sensitized Type 304 stainless steel in high purity water. These data were obtained via the constant extension rate test (CERT) [20].
trolling the oxygen content during the start-up and steady state is now becoming a major remedy for BWR pipe cracking [133].

2.3.3.2 Effect of pH and Impurity

There is growing evidence that environmental impurities (sulfates, chlorides, carbonates, etc.) may strongly accelerate the initiation and propagation stages of stress corrosion cracking [135]. Decomposition of cationic demineralizer resins in high temperature water (\(> 150^\circ\text{C}\)) or in radiolytic fields is believed to be one of the major sources in releasing acid sulfate and acid chloride impurities [136-138].

In sensitized stainless steels, most impurities act to accelerate IGSCC. However, some impurities in pure water may induce transgranular SCC of annealed stainless steel. Andresen [139] and Hishida and Nakada [11] have observed this phenomenon in water containing chloride using a constant extension rate test at 288 \(^\circ\text{C}\). The latter investigators demonstrated that, in lightly sensitized Type 304 stainless steel, the elongation to failure in "non-deaerated" pure water was 48%. This value drops to 32% and to 11% when chloride increases to 0.5 ppm and to 1 ppm, respectively.

The influence of diluted sulfuric acid in 289 \(^\circ\text{C}\) water with different amounts of dissolved oxygen and hydrogen was studied by Ruther et al. [101] in a constant-extension-rate test. The result indicated that the diluted sulfuric acid
solution (with sulfate content below 0.1 ppm) has a strong detrimental effect in promoting IGSCC in the lightly sensitized (700 °C/0.5 hr + 500 °C/24 hr) specimen when the solution with dissolved oxygen and hydrogen is higher than 0.2 ppm and 0.5 ppm, respectively. On the other hand, in a medium sensitized specimen, a moderate detrimental effect of the sulfuric acid was observed in the solution with 0.2 ppm dissolved oxygen or with 0.5 ppm dissolved hydrogen. This detrimental effect was not observed in the solution with 0.8 ppm oxygen (see Figure 2-34) [101]. No satisfactory explanation has been made for these phenomena.

Recently, the effect of sulfuric acid in 288 °C high purity water was also studied by Andresen [135]. By using shallow grooved compact tension specimens, he observed only small variations in the threshold stress intensities and crack growth rates of the tested specimens as a function of impurity level. Again, no explanation has been made for this observation. However, by using constant extension rate test specimens, Andresen discovered that the average crack propagation rates were higher in the presence of acidic, neutral, or basic impurities than in pure water, as shown in Table 2-5 [135]. These results suggest that the intergranular mode is promoted in impure water. A possible explanation made by Andresen is that the rate determining step in high temperature solutions is liquid diffusion. However, the addition of foreign anions can displace the OH anion to
Figure 2-34. Influence of dissolved gases and sulfuric acid in 289 °C water on the time to failure of Type 304 specimens sensitized a) at 700 °C/0.5 hr + 500 °C/24 hr (EPR value = 2 °C/cm²), and b) at 700 °C 24 hr (EPR value = 20 °C/cm²) [101].
### Table 2-5
Average Crack Propagation Rates in CERT Tests on Sensitized Type 304 Stainless Steel

<table>
<thead>
<tr>
<th>SPECIMEN</th>
<th>ENVIRONMENT</th>
<th>288°C</th>
<th>pH</th>
<th>$x10^{-7}$</th>
<th>% εt(3)</th>
<th>% εf</th>
<th>AVERAGE a (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A13</td>
<td>Pure Water</td>
<td>Neutral</td>
<td>3.3</td>
<td>5.3</td>
<td>17.4</td>
<td>3.7 x 10^{-7}</td>
<td></td>
</tr>
<tr>
<td>A25</td>
<td>10μS HCl/H₂SO₄(4)</td>
<td>Acid</td>
<td>3.3</td>
<td>2.7</td>
<td>10.6</td>
<td>8.7 x 10^{-7}</td>
<td></td>
</tr>
<tr>
<td>A26</td>
<td>10μS H₂SO₄</td>
<td>Acid</td>
<td>3.3</td>
<td>2.6</td>
<td>7.8</td>
<td>1 x 10^{-6}</td>
<td></td>
</tr>
<tr>
<td>A27</td>
<td>10μS NaHSO₄</td>
<td>Neutral</td>
<td>3.3</td>
<td>5.0</td>
<td>9.7</td>
<td>2.6 x 10^{-6}</td>
<td></td>
</tr>
<tr>
<td>A39</td>
<td>10μS NaCl</td>
<td>Neutral</td>
<td>3.3</td>
<td>5.1</td>
<td>9.8</td>
<td>2.3 x 10^{-6}</td>
<td></td>
</tr>
<tr>
<td>A30</td>
<td>10μS Na₂SO₄</td>
<td>Basic</td>
<td>3.3</td>
<td>6.2</td>
<td>12.2</td>
<td>1.7 x 10^{-6}</td>
<td></td>
</tr>
<tr>
<td>A12(5)</td>
<td>Pure Water</td>
<td>Neutral</td>
<td>3.3</td>
<td>9</td>
<td>22</td>
<td>3.8 x 10^{-7}</td>
<td></td>
</tr>
<tr>
<td>A11</td>
<td>55μS H₂SO₄</td>
<td>Acid</td>
<td>0.53</td>
<td>2.8</td>
<td>4.8</td>
<td>5.6 x 10^{-7}</td>
<td></td>
</tr>
<tr>
<td>A19(6)</td>
<td>55μS H₂SO₄</td>
<td>Acid</td>
<td>0.53</td>
<td>3.2</td>
<td>4.8</td>
<td>2.1 x 10^{-6}</td>
<td></td>
</tr>
<tr>
<td>A22(6)</td>
<td>10μS HCl/H₂SO₄(4)</td>
<td>Acid</td>
<td>0.53</td>
<td>2.7</td>
<td>4.3</td>
<td>6.4 x 10^{-7}</td>
<td></td>
</tr>
<tr>
<td>A28(6)</td>
<td>10μS H₂SO₄</td>
<td>Acid</td>
<td>3.3</td>
<td>4.2</td>
<td>10.4</td>
<td>1 x 10^{-5}</td>
<td></td>
</tr>
</tbody>
</table>

(1) Based on Actual Test Time from Estimated Initiation to Failure
(2) Welded 10"D Schedule 80 Pipe (BS5656) Heat Treated at 500°C/24 hr in Vacuum Run in 288°C Water Containing 0.2 ppm O₂ (See (26,13/))
(3) % εt (Strain to Initiation) is Based on Repeated Interrupted CERT Tests
(4) 0.5 ppm HCl + 0.46 ppm H₂SO₄
(5) Tested at 200°C
(6) Tested under hydrogen water chemistry conditions of: 125 ppb H₂, 40 ppb O₂
accelerate cracking kinetics (see Figure 2-35) [135].

2.3.3.3 Effect of Electrochemical Potential

Because the BWR environment contains hydrogen peroxide and hydrogen as well as oxygen, stress corrosion experiments conducted in high purity water with various oxygen-temperature combinations may not accurately reproduce the BWR environment. One approach to simulating BWR environments in the laboratory is to control the electrochemical potential [123]. This approach requires a high temperature reference electrode and the presence of a diluted electrolyte, such as 0.01 N sodium sulfate. The basic assumptions are that the ECP is the dominating parameter that determines whether IGSCC will occur and that measurements of the ECP in operating BWRs automatically take into account the amount of hydrogen peroxide, oxygen, and hydrogen present. As shown in section 2.1.1.2 and Figure 2-3(d), the ECP, occurring in BWRs at a temperature between 250 °C and 290 °C, is between -0.4 and 0 V_{SHE}. Therefore, this potential range is most important in studying the susceptibility of IGSCC in sensitized Type 304 stainless steel. On the other hand, the systematic study of Indig and McIlree [159] on the effect of dissolved oxygen concentration on the corrosion potential of Type 304 stainless steel in high purity water at 274 °C, as shown in Figure 2-36 [159], revealed that the corresponding oxygen content at the potential range between -0.4 and 0 mV_{SHE} is in the range of 10 ppb and 10 ppm. The majority
Figure 2-35. Schematic of an active crevice or crack showing that, with impurities present, concentration of both the anion impurity and hydrogen ion is possible. This could result in acceleration of cracking kinetics [135].
Figure 2-36. The effect of dissolved oxygen concentration on the corrosion potential of Type 304 stainless steel in high purity water at 274 °C [159].
of oxygen controlled studies were also conducted in that oxygen content range.

Cowan and Kaznoff [141] were among the first to report that stress samples, polarized in dilute sodium sulfate solutions at 288 °C to a potential equivalent to that occurring in BWRs environment (about 300 mV$_{SHE}$), crack intergranularly in times similar to those observed in BWR environments. Later on, several SCC tests (on differently prepared specimens) were carried out in the same type of solution at various potentials [142, 159]. Vermilyea [142] observed IGSCC in furnace sensitized Type 304 and 302 stainless steel using notched, creviced, and smooth specimens exposed to 0.01 M sodium sulfate solutions at 0 and 250 mV$_{SHE}$ and at 288 °C. Indig and McIlree [159] also found IGSCC at -300 mV$_{SHE}$ and -100 mV$_{SHE}$, but no cracking was observed at -400 mV$_{SHE}$. For welded plus LTS samples (500 °C/24 hr), IGSCC was observed at -450, -400 and -100 mV$_{SHE}$.

More complete studies of SCC susceptibility as a function of potential in sodium sulfate solutions were performed by Cragnolino and Agrawal [143] at 250 °C, Hishida et al. [144] at 290 °C, and Yonezawa and Tsuruta [3] at 300 °C. Figure 2-37 [143] shows the results of the slow strain rate tensile test vs. potential in deaerated 0.01 M sodium sulfate solutions and in pure water with and without dissolved oxygen at 250 °C. The specimen was lightly sensitized (650 °C/1 hr). As revealed in the figure, at applied
Figure 2-37. Ratio of time to failure in 0.01 M sodium sulfate and high purity water to that in argon at 250 °C as a function of potential and anodic polarization curve for sensitized Type 304 stainless steel [143].
potentials more anodic than $-300 \text{ mV}_{\text{SHE}}$, the sensitized Type 304 stainless steel is susceptible to IGSCC. The cracking seems to be most severe at $-100 \text{ mV}_{\text{SHE}}$. A similar behavior has been observed in air-saturated pure water. Yonezawa and Tsuruta [3] observed essentially the same results using slow strain rate and constant load tests in a more concentrated sodium sulfate solution and at a higher temperature. The results mentioned above seem to support the argument that the key parameter for IGSCC is the electrochemical potential, regardless of whether the source is internally dissolved oxygen or under external electronic control.

However, it is important to note, as was pointed out by Indig and McIlree [159], that the limiting potential for the IGSCC of sensitized Type 304 stainless steel is not a constant value but depends on the microstructure and probably also on the particular heat of the stainless steel employed. Nevertheless, there exists a critical potential below which IGSCC does not occur. According to the results of different authors [143-146, 159], this range is from $-450$ to $-370 \text{ mV}_{\text{SHE}}$. As suggested by Szklarska-Smialowsak and Cagnolino [3], this critical potential seems to correspond to a potential value at which acidification of grain boundaries is high enough to cause a fast dissolution of oxide film at the Cr-depleted zone.

In controlled potential tests [10, 14, 147, 148], IGSCC has been observed [10] in 0.01M NaCl at 250 °C within a
potential range equivalent to that obtained in sulfate solutions. The rate of crack propagation in chloride solutions was found to be similar to that found in sulfate solutions. At lower temperatures, around 100 °C, the slow strain rate tests conducted by Ford and Silverman [149] in sodium sulfate and sodium chloride solutions have revealed the occurrence of IGSCC within a narrow range of potentials, namely from 150 to 220 mV_{SHE}. As was mentioned before, IGSCC has also been observed in pure water with about 2 ppm oxygen, and this corresponds to the same potential region. In all these environments, the rate of crack propagation was almost identical, as shown in Figure 2-38 [149]. This seems to indicate that the rate of localized acidification of the metal surface is comparable in these environments. Finally, the study of Lin et al. [14], using slow strain rate tests under potential control in 0.01M NaCl at temperatures ranging from 100 °C to 250 °C, proposed that, for the temperatures they studied, the rate determining step of IGSCC in sensitized Type 304 stainless steel is a diffusion process. The apparent activation energy of this process has a value of 28 ± 12 kJ/mol (Figure 2-39) [14].
Figure 2-38. Estimated crack propagation rate of sensitized Type 304 stainless steel in 0.01 M sodium sulfate and in oxygenated pure water at about 100 °C [149].
Figure 2-39. Average intergranular crack propagation rates as functions of temperature for sensitized Type 304 stainless steel in 0.01 M NaCl solution [14].
2.4 Crack Growth Rate Study by Fracture Mechanics

2.4.1 Brief Review of Fracture Mechanics

The conventional design criteria are based on tensile strength, yield strength and buckling stress. These criteria are adequate for many engineering structures, but they are insufficient when there is the likelihood of cracks. Now, after approximately three decades of development, fracture mechanics has become a useful tool in the design of material used in critical environments.

Currently, the only method approved by ASME Code and federal regulations dealing with nuclear power plants for the quantitative evaluation of the critical condition for component failure to occur is linear elastic fracture mechanics (LEFM) [160]. In LEFM, all deformation is assumed to be elastic, and structural instability is usually assumed to occur when the stress intensity factor, $K$, due to the applied load exceeds a critical value at which crack growth initiates. These assumptions are appropriate for perhaps 60 to 70% of all engineering situations of practical importance and accordingly, LEFM-based analyses are expected to gain increasingly wide acceptance by code and regulatory bodies. In an additional 20% of the cases of interest, extensive plastic deformation occurs prior to structural instability. LEFM predictions can be excessively conservative in such cases and a new branch of fracture mechanics, elastic-plastic and general-yielding fracture mechanics, is being
developed to provide an accurate predictive capability for ductile fracture [161-163]. The remaining 10 to 20% of structural analysis problems involve time-dependent deformation and creep fracture processes. This is a much less developed area of fracture mechanics.

Linear elastic fracture mechanics (LEFM) considers only the linear elastic response of the material. Thus, for both loading and unloading, the stresses and strains are related linearly, as shown in Figure 2-40(a). The solutions to the equations for the elastic response of cracked bodies contain a stress field close to and surrounding the crack tip that lends itself to a one-parameter description, as in Figure 2-41 [164, 165]. This field, identified as the K-field, is shown schematically in Figure 2-42 [160]. Under plane strain loading conditions, the elastic stresses and strains within this field are completely described by the parameter K, the appropriate stress intensity factor. By definition, K is related to the nominal applied stress (σ) and the crack size, a, by a relation of the form

\[ K = Y \frac{\sigma}{\pi a} \]  
Eqn. 2-1

where Y is a function of the component geometry and the way the component is loaded.

The ability of the material to support a K-field of a given intensity without crack extension is characterized by the critical value of K, which is denoted by a material
Figure 2-40. Schematic representation of the different types of stress-strain relations: a) linear elastic; b) elastic-plastic [160].
Figure 2-41. Characterization of stress at a crack tip in a body loaded in Mode I. The Westergaard stress equations [164] are shown for the stress in the X and Y directions [165].
Figure 2-42. Schematic representation of the stress fields of cracked bodies: a) linear elastic behavior; b) linear elastic behavior with small scale yielding; c) large-scale yielding [160].
property called the fracture toughness, $K_{IC}$. Specifically, $K_{IC}$ is that value of $K_I$ corresponding to the onset of crack extension in a specimen with a thickness sufficient to give plane strain conditions. For thin structures where plane stress conditions occur, the appropriate toughness is designated $K_C$, and $K_C > K_{IC}$. The sample thickness criterion for plane strain and plane stress is shown in Figure 2-43 [166].

The one-parameter description of the crack tip stress field provided by $K$ has proved to be useful in characterizing subcritical crack growth processes as well as instability. For many materials in many environments, it has been found that the rate of fatigue crack growth, $da/dN$, can be related over a wide range of the mode I stress intensity, $K_I$, by a simple power function of the type [167]

$$\frac{da}{dN} = C(\Delta K_I)^n \quad \text{Eqn. 2-2}$$

where the constants $C$ and $n$ depend on both the material and the environment. In addition, it has been found that stress corrosion crack growth is often controlled by $K_I$ rather than by the nominal applied stress [176]. For instance, Novak and Rolfe [176] showed that crack growth due to stress corrosion would not occur under linear elastic/plane strain conditions unless $K_I$ exceeded a threshold value termed $K_{ISCC}$. Thus, when the stress distribution ahead of the crack can be accurately characterized by $K$, LEFM can provide the basis
Figure 2-43. Relative plastic zone sizes for bodies in plane strain (at left) and in plane stress (at right) [166].
for both the crack growth analysis and the flaw evaluation analysis.

The elastic analysis, however, must be reconciled with the existence of a plastic zone. The size of this zone, shown schematically in Figure 2-42(b), is related to the normal net section stress ($\sigma$) at the onset of crack extension. As long as $\sigma$ is less than about 60% of the yield strength (this criterion is essentially the same as the thickness criterion shown in Figure 2-43), the plastic zone is smaller than the K-field. Under these conditions, $K_I$ dominates the solution for the plastic zone. Consequently, the LEFM analysis is valid for this specimen.

When the material is tough and exceeds 60% of the yield strength, the plastic zone existing at the moment of crack extension is larger than the K-field. The J integral [168-171] was introduced by Rice et al [168-170] to characterize the stress-strain conditions existing at the crack tip. Briefly, the J integral is based on the non-linear stress-strain curve shown in Figure 2-42(b) and the region described by the J integral is identified as the J-field in Figures 2-42(b) and 2-42(c). The J-integral value at the onset of crack extension provides a fracture toughness parameter, $J_{IC}$, in the elastic-plastic deformation region. More general and fundamental information about the LEFM and J-integral can be found in various fracture mechanics textbooks [165, 172-174].
2.4.2 Specimen for Stress Corrosion Study

Pre-cracked specimens are widely used for fracture mechanics studies. These types of specimens provide a flaw geometry for which a stress analysis is available through fracture mechanics. In addition, especially for stress corrosion testing, they eliminate the uncertainties associated with the initiation of SCC (e.g. growth of a corrosion pit), and produce stress corrosion data that are potentially more useful for predicting the behavior of large structural components for which fracture is a critical design factor [28].

Many different types of pre-cracked specimens for mechanical and corrosion testing are available. Figure 2-44 [28] demonstrates the great variety of these specimens. Generally, these specimens are classified with respect to the relationship between the stress intensity factor, $K$, and crack extension. According to the method of stressing and/or the geometry of the specimen, the fracture mechanics specimens may be divided into three categories [28]:

1. Constant $K$ Type specimen.
2. Increasing $K$ Type specimen.
3. Decreasing $K$ Type specimen.

The constant $K$ Type specimens, which are also called contoured double cantilever beam (contoured DCB) specimens, have often been employed for fundamental studies of subcritical crack growth because the independence of $K$ on crack
Figure 2-44. The types of fracture mechanics-type specimens available for mechanical and corrosion testing [28].
extension enables researchers to control the history of stress intensity on the test piece. In order to maintain a constant K value with crack extension, the beam of the specimens is shaped so that there is a linear relationship between specimen compliance and crack length.

In the second category, the pre-cracked specimens, the increasing K Type specimen, are usually stressed under constant load conditions in tension or bending. The stress intensity factor increases as the crack propagates. This type of specimen is widely adopted for studying the SCC growth rate of material in different environments at the Stage II region of the crack growth characteristic curve (Figure 2-11) [100, 101, 135].

In the last category of pre-cracked specimens, the decreasing K Type specimen, where $K_I$ decreases with crack extension, specimens are mostly stressed under conditions of constant extension. Crackline-loaded, single-edge-cracked plate specimens are maintained at a constant crack-opening displacement by a bolt, wedge, or other devices. The overall result of this procedure is to cause the load to diminish and, consequently, the $K_I$ to decrease as the crack extends under the influence of an aggressive environment. This type of specimen is most suitable for studying the crack growth rate at the Stage I region of the crack growth curve, as well as the $K_{ISSC}$ value, of material in different corrosive environments [103]. The specimen used in this
present study, the modified wedge opening loading (WOL) specimen, belongs in this category. Details of the modified WOL will be discussed in the next section.

Crack plane orientation is also an important consideration in designing a fracture mechanics specimen. Its nomenclature is presented in Figure 2-45. The T-L orientation is used in this current work.

2.4.3 Modified Wedge-Opening-Loading (WOL) Fracture Specimen and Analysis

2.4.3.1 Introduction

The original WOL fracture specimen was developed by Manjoine [175]. The specimen was designed for dead-weight loading, as shown in Figure 2-46 [176] (an increasing K Type specimen). Subsequently, in order to eliminate the need for the large testing fixtures required for this type of specimen, as well as to reduce the number of specimens required to determine a \( K_{ISCC} \) value, Novak and Rolfe (r153) modified the loading mechanism of the WOL specimen by the use of a bolt and loading tup, as shown in Figure 2-47 [176]. In this loading mechanism, the modified WOL specimen can be self-stressed without using a tensile machine or any external load.

Basically, the crack opening of a modified WOL specimen is fixed by the bolt, and the loading is carried out by a constant displacement (rather than by a constant load as in the original design). Because a constant crack-opening
Figure 2-45. Nomenclature used to denote crack-plane orientation in specimens used for mechanical or corrosion testing [28].
Figure 2-46. Schematic of the Wedge-Opening-Loading (WOL) specimen [176].
Figure 2-47. Schematic showing basic principle of the modified WOL specimen [176].
displacement (COD) is maintained throughout the test, the
force, P, decreases as the crack length increases. In
cantilever-beam testing, the $K_I$ value increases which leads
to fracture for each specimen. In contrast, in the modified
WOL specimen, the $K_I$ value decreases which leads to crack
arrest. The effect of the decrease in P more than co pepen­
sates for the increase in $a$. A comparison of these two
types of behavior is shown in Figure 2-48 [176]. Thus, only
a single specimen is required to establish the $K_{ISCC}$ level
because $K_I$ approaches the limiting value of $K_{ISCC}$ at suffi­
ciently long time. However, duplicate specimens are usually
tested to demonstrate reproducibility [176].

2.4.3.2 Stress Intensity Analysis

Since the modified WOL specimen has exactly the same
geometry as the originally designed WOL specimen, the stress
intensity factor calculated for the WOL specimen is the same
as that for the modified WOL specimen. According to Wessel
[177], for the WOL specimen geometry, the stress intensity
is represented as:

$$K_I = \frac{P C_3}{(B B_N)^{1/2} a^{1/2}}$$

Eqn. 2-3

where:

- $P$ = load
- $B$ = specimen thickness
- $B_N$ = net thickness of the side grooved specimen
- $a$ = total crack length (includes the notch length
  and the fatigue precrack length)
Figure 2-48. Difference in behavior for the modified WOL and cantilever-beam specimens [176].
$C_3 = \text{function of } (a/W)$
$W = \text{specimen depth.}$

The functional dependence of $C_3$ on $a/W$ is expressed in terms of the following polynomial relationship:

$$C_3 = [30.96(a/W) - 195.8(a/W)^2 + 730.6(a/W)^4$$
$$-1186.3(a/W)^4 + 754.6(a/W)^5]$$  \text{Eqn. 2-4}

Equation 2-3 was obtained by the boundary value collocation [178, 179], and equation 2-4 is a polynomial fit to specific analytically derived values [179, 180]. The calculated values for $C_3(a/W)$ are given in Table 2-6.

On the other hand, the compliance calibration of the modified WOL specimen was first made by Novak and Rolfe [176]. Using smooth and face-grooved (5%) specimens machined from an 18Ni maraging steel with a yield strength of 251 ksi, they measured the elastic compliance as a function of the relative crack length ($a/w$). These data were then normalized with respect to specimen thickness, $B$, and modulus of elasticity, $E$, and a curve was fitted to the data by using a computer. The resulting equation was of the form

$$EB \frac{\nu}{F} = C_6$$  \text{Eqn. 2-5}

where, for a smooth specimen,

$$C_6 = \exp [4.495 - 16.130(a/W)^2 - 89.125(a/W)^3$$
$$+ 46.815(a/W)^4]$$  \text{Eqn. 2-6}
Table 2-6 Tabulation of $C_3$ and $C_6$ for Calculation of $K_1$ from COD Compliance-Calibration Values

<table>
<thead>
<tr>
<th>$\frac{a}{W}$</th>
<th>$C_3 \frac{a}{W}$</th>
<th>$C_6 \frac{a}{W}$</th>
<th>Smooth</th>
<th>5% Face-Notched</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.300</td>
<td>3.617</td>
<td>20.22</td>
<td>29.49</td>
<td></td>
</tr>
<tr>
<td>0.320</td>
<td>3.800</td>
<td>31.23</td>
<td>31.86</td>
<td></td>
</tr>
<tr>
<td>0.340</td>
<td>4.183</td>
<td>33.57</td>
<td>34.51</td>
<td></td>
</tr>
<tr>
<td>0.360</td>
<td>4.494</td>
<td>36.24</td>
<td>37.44</td>
<td></td>
</tr>
<tr>
<td>0.380</td>
<td>4.824</td>
<td>39.25</td>
<td>40.65</td>
<td></td>
</tr>
<tr>
<td>0.400</td>
<td>5.172</td>
<td>42.61</td>
<td>44.16</td>
<td></td>
</tr>
<tr>
<td>0.420</td>
<td>5.541</td>
<td>46.32</td>
<td>47.97</td>
<td></td>
</tr>
<tr>
<td>0.440</td>
<td>5.932</td>
<td>50.40</td>
<td>52.11</td>
<td></td>
</tr>
<tr>
<td>0.460</td>
<td>6.350</td>
<td>54.87</td>
<td>56.58</td>
<td></td>
</tr>
<tr>
<td>0.480</td>
<td>6.801</td>
<td>59.74</td>
<td>61.44</td>
<td></td>
</tr>
<tr>
<td>0.500</td>
<td>7.203</td>
<td>64.07</td>
<td>66.72</td>
<td></td>
</tr>
<tr>
<td>0.520</td>
<td>7.836</td>
<td>70.88</td>
<td>72.49</td>
<td></td>
</tr>
<tr>
<td>0.524</td>
<td>8.443</td>
<td>77.27</td>
<td>78.83</td>
<td></td>
</tr>
<tr>
<td>0.506</td>
<td>9.131</td>
<td>84.33</td>
<td>85.87</td>
<td></td>
</tr>
<tr>
<td>0.580</td>
<td>9.920</td>
<td>92.19</td>
<td>93.76</td>
<td></td>
</tr>
<tr>
<td>0.600</td>
<td>10.831</td>
<td>101.05</td>
<td>102.72</td>
<td></td>
</tr>
<tr>
<td>0.620</td>
<td>11.892</td>
<td>111.16</td>
<td>113.02</td>
<td></td>
</tr>
<tr>
<td>0.640</td>
<td>13.134</td>
<td>122.89</td>
<td>125.06</td>
<td></td>
</tr>
<tr>
<td>0.660</td>
<td>14.591</td>
<td>136.69</td>
<td>139.35</td>
<td></td>
</tr>
<tr>
<td>0.680</td>
<td>16.305</td>
<td>153.24</td>
<td>156.59</td>
<td></td>
</tr>
<tr>
<td>0.700</td>
<td>18.321</td>
<td>173.44</td>
<td>177.74</td>
<td></td>
</tr>
<tr>
<td>0.720</td>
<td>20.688</td>
<td>198.57</td>
<td>201.17</td>
<td></td>
</tr>
<tr>
<td>0.740</td>
<td>23.462</td>
<td>230.44</td>
<td>237.77</td>
<td></td>
</tr>
<tr>
<td>0.760</td>
<td>26.707</td>
<td>271.71</td>
<td>281.33</td>
<td></td>
</tr>
<tr>
<td>0.780</td>
<td>30.488</td>
<td>326.28</td>
<td>338.93</td>
<td></td>
</tr>
<tr>
<td>0.800</td>
<td>34.882</td>
<td>400.11</td>
<td>416.73</td>
<td></td>
</tr>
</tbody>
</table>

* For 1-7 WOL specimens with $(H/W) = 0.436$
and for a 5 per cent face notched specimen,

\[
C_6 = \exp \left[ 3.453 - 8.097(a/W) + 42.314(a/W)^2 
- 64.677(a/W)^3 + 36.845(a/W)^4 \right]
\]  
Eqn 2-7

Combining equations 2-3 and 2-5, the \( K_I \) values of the modified specimen can be calculated by knowing the COD of the specimen.

\[
K_I = \frac{E B V C_3}{C_6(B N_{in})^{1/2} a^{1/2}}
\]  
Eqn 2-8

where \( V = \) crack opening displacement (COD)

Much research has been done more recently [180, 183] in order to obtain a better analytic expression for the stress intensity factor, \( K \), and compliance, \( C \), for the modified WOL specimen. For example, Newman [183] pointed out that previous boundary collocation procedures [185, 186] ignored the effects on \( K \) due to pin loaded holes. He therefore proposed a new expression for \( K \).

\[
K = \frac{P}{B W^{1/2}} \left[ 4.55 - 40.32(a/W) + 414.7(a/W)^2 - 1698(a/W)^3 
+ 3781(a/W)^4 - 4287(a/W)^5 + 2017(a/W)^6 \right]
\]  
Eqn 2-9

for \( a/W \) between 0.2 and 0.8

where \( P, B, a, \) and \( W \) are the same as previously defined.

Subsequently, Bowie et al. [184] further proposed a three parameter fit which yielded a promising new numerical approximation to tabulate normalized compliance and \( a/W \).
values. More recently, Lefort and Mowbray [181], using finite element and experimental compliance studies, have redefined a new set of analytical solutions for face-grooved (5%) specimens.

\[ K_I = V E (a/W)^{1/2} \exp \left[ 0.8554 - 7.7483(a/W) 
+ 6.77372(a/W)^2 - 2.80996(a/W)^4 \right] \quad \text{Eqn. 2-10} \]

where \( V, E, a \) and \( W \) are the same as previously defined.

Since the \( a/w \) ratio used in this study is between 0.38 and 0.45, the compliance derivative calibration made by Lefort and Mowbray [181] and Ryder et al. [180] indicates that, in that \( a/w \) range, the difference between the analytical and experimental displacement calibration is negligible (within 5%). Therefore, for convenience, the equations developed by Novak and Rolfe were selected in this present study to calculate the stress intensity and crack-opening-displacement. The equation developed by Lefort and Mowbray was also used as a reference to calculate the \( K_I \) value.

2.4.4 Crack Growth Rate Measurement of Modified WOL Specimens in Autoclaves

There are three major requirements in the characterisation of cracked test specimens by linear elastic fracture mechanics (LEFM). It is necessary to know the compliance of the specimen, the crack length, \( a \), and the applied load, \( P \). However, for the modified WOL specimen, because the specimen is loaded under a constant deflection condition, as well
as the compliance of the specimen being well defined, only one of the requirements mentioned above (either crack length, \(a\), or load, \(P\)) is needed to compute the other parameters. For example, as shown in Figure 2-49, knowing the load, \(P\), of the specimen, one can calculate the \(K_1\) value from equation 2-3, and the crack length from equation 2-5. On the other hand, knowing the crack length, \(a\), the \(P\) and \(K\) values can be calculated using equations 2-5 and 2-7, respectively.

In the literature, the methods available for measuring crack length may be broadly classified as optical, mechanical and electrical. A brief summary of this method is given in Table 2-7 [187]. Also in the table, some of the relative advantages and disadvantages of the various methods are listed in note form. The combination of environment and specimen design used in this study immediately eliminated almost all of the techniques described in the table. Direct optical observation, Eddy-current measurement, ultrasonic techniques, and acoustic emission are all impossible inside an autoclave. COD measurement and dc potential drop are not suitable for decreasing \(K/\)constant COD tests. The interpretation of ac potential measurements to predict crack shape is complicated by the "skin effect". Strain gage filaments are also not well suited for high temperature aqueous environments.
Figure 2-49. Schematic relation between the load, $P$, the crack opening displacement (COD), $V$, and the crack length, $a$, in the modified WOL specimen [176].
### Table 2-7

**Methods of Crack Length Measurement**

<table>
<thead>
<tr>
<th>Technique</th>
<th>Brief Description</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Optical</strong></td>
<td>Relies on microscopes or telescopes - often aided by etched or etched markings. Almost all test piece geometries.</td>
<td>Inexpensive. Does not require calibration. Does not require specimen to behave in a linear elastic manner.</td>
<td>Only gives surface readings - usually understates average crack length because of crack curvature. Susceptible to misalignment and hence time consuming. Requires surface to be accessible and in well polished condition.</td>
</tr>
<tr>
<td><strong>Mechanical Methods</strong></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>(a) Crack opening displacement (COD)</td>
<td>Basis is to measure COD usually between points along the loading line or, in the case of bond and wedge opening loading specimens, at the front face (von Stetten and Truesley, 1967; Sullivan and Freed, 1972; Nanami and James, 1974; Sullivan, 1975; Huberty, 1971 and Sullivan and Chohr, 1977). Displacements measured most often by clip gauges or linear voltage displacement gauges. For high temperature testing extensions may be used to transfer the displacements to lower temperature regime for measurement. Linearity extension zone may be used via moving scales to measure displacements inside enclosures. Any test piece geometry that behaves in a linear elastic manner.</td>
<td>Cost depends on application. Ranges from low cost in room temperature air to moderately expensive in high temperature aggressive environments. The method does not require the specimen to be visually accessible and can provide an average crack length figure. Easily incorporated in automatic systems.</td>
<td>Calibration required for test pieces other than C.T. and Tripyt WOL specimens. (Refer to the discussion, Section 5, for more details.)</td>
</tr>
<tr>
<td>(b) Back-face strain</td>
<td>This is the subject of the present communication. Strains measured on the back-face of C.T. or Tripyt WOL specimens by strain gauges or possibly clip gauges or transducers in the case of large test pieces. Possible use in single edge notched tension or 3 and a point bend specimens. All specimens must behave in a linear elastic manner.</td>
<td>Cost depends on application. Ranges from very inexpensive in room temperature air tests to moderately expensive in high temperature aggressive environments. Method does not require the specimen to be visually accessible and can provide an average crack length figure. Shows excellent characteristics for incorporation in automatic systems (Refer to the discussion, Section 5, for more details).</td>
<td>Calibration required for test pieces other than C.T. and Tripyt WOL specimens. (Refer to the discussion, Section 5, for more details.)</td>
</tr>
<tr>
<td><strong>Electrical Methods</strong></td>
<td>Electrically conducting wires are attached to the specimen in such a way that they are broken by an advancing crack providing simple changes in resistance (Lee, 1969; Tomlinson and Anderson, 1961; Collins, 1961). Can be used for all specimen geometries.</td>
<td>Low cost. Easily adapted for automatic processes.</td>
<td>Only gives surface readouts. Not well suited for high temperature and aggressive environments. Difficult to locate gauges and ensure that the element is always broken by the presence of the crack tip and only the crack tip.</td>
</tr>
</tbody>
</table>

To be continued
<table>
<thead>
<tr>
<th>Technique</th>
<th>Brief Description</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrical Methods</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) d.c. potential drop (resistance)</td>
<td>A constant d.c. current is passed through a specimen in such a way that a charge in crack length alters the potential difference of suitably placed contact points usually in vicinity of the crack tip. (Belyakov and Kasse 1963, Stanley and Brown 1965, Brown and Stanley 1963, Gilley and Pearson 1954, and McIntyre 1954). Suitable for all test piece geometries.</td>
<td>Low cost. Does not require very delicate instrumentation attached to the specimen. High stability for long-term tests and some relaxation from linear elastic behaviour easily accommodated. Particularly well suited for automatic control and long-term, high-temperature testing (Heigh and Richards, 1975). Robust and simple. Can give an average crack length value.</td>
<td>Some theoretical calibrations available, but usually in carry out calibration tests. Some uncertainty in stress corrosion and corrosion fatigue studies over possible interference with electrochemical conditions adjacent to crack tip. For decreasing or constant SID tests crack faces may short electrically thus under-estimating crack length. Bridging of crack surfaces by corrosion products may produce erroneous crack length readings. In some cases the grips may have to be electrically isolated from the testing machine. Can be suited for very large specimens.</td>
</tr>
<tr>
<td>(c) a.c. potential drop (resistance)</td>
<td>Similar to (a) above.</td>
<td></td>
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<tr>
<td>(d) Eddy-currents</td>
<td>An ac current probe positioned adjacent to a strained surface produces an electrical signal indicating the crack (Lauth et al., 1965). Can be used with a conventional oscilloscope that moves the probe in such a way that a null eddy current signal is maintained. Need for centre crack sheets but should be adaptable to other geometries.</td>
<td>Can be easily adopted for automatic processes.</td>
<td>May only be useful for surface measurements. Expense.</td>
</tr>
<tr>
<td>(e) Ultrasonic technique</td>
<td>Involves transmission and reception of a high frequency sound wave intersected by a crack (Clark, 1967). If probe is fixed the moving crack alters the propagation of the signal reflected by each and the opposite boundary of the specimen. A more accurate version involves a stepping motor that moves the probe such that the strength of the signal reflected by the crack remains constant (Clark and Craighead, 1963). Read exactly on wedge opening loading type compact specimens. Can be adapted into automatic processes. External measurements of crack length. Only method that can give crack profile. Relaxation from linear elastic behaviour easily accommodated.</td>
<td>Can be adapted into automatic processes. Internal measurements of crack length. Only method that can give crack profile. Relaxation from linear elastic behaviour easily accommodated.</td>
<td>Not well suited for small, thin specimens. Expense. Cannot be used at high temperatures. Not well suited in environmental testing. Not a proven technique for specimens other than wedge opening loading type compact specimens. Difficult to achieve high resolution.</td>
</tr>
<tr>
<td>(f) Acoustic emission</td>
<td>Involves attenuation of acoustic transducer in contact with test piece which oscillates at its resonant frequency on exciting elastic stress waves from source of deformation (Clayton and Brown 1955). The detected emissions are then amplified, selectively filtered and conditioned and then counted either as a period or to a rate of emission or as a cumulative total. Adaptable to any geometry.</td>
<td>Can be very sensitive for detecting onset of cracking.</td>
<td>Expensive, sophisticated equipment. Filtering of extraneous noise from test machine and grips etc. necessary during testing. Poor correlation with crack length and signals are material dependent.</td>
</tr>
</tbody>
</table>
The only technique left on the list is the back-face strain technique. Recently, Deans and Richards [187] and Mukherjee et al. [188, 189] adopted this technique in monitoring crack growth rates of modified WOL specimens in a high pressure gas chamber. The strain gage was attached either on the back surface or the side surface of the specimen, as shown in Figure 2-50. These workers both found that the strain signals measured from strain gages attached to the specimen surface changed linearly with the crack length, as in Figure 2-51 [189]. Therefore, by monitoring the variation of strain with time, the crack growth rate and the stress intensity at the crack tip can be calculated. For the high temperature autoclave system, they suggested using weldable strain gages instead of regular chemical-bonded strain gages. The advantage of this method is the simplicity of the design. The main disadvantage is that the weldable strain gage (cost about $500.00) is not reusable. In addition, the strain variation of the strain gage is limited in this type of arrangement. The strain which is measured by the strain gage only changes about 400 micro-strain when the crack propagates one inch (convert from Figure 2-51). Therefore, this method is only good in monitoring a crack growth rate of the WOL specimen higher than $10^{-10}$ m/sec.

Because, in the present study, the expected crack growth rate is between $10^{-10}$ m/sec and $10^{-11}$ m/sec, a new
Figure 2-50. The strain gauge placement for the modified WOL specimen by using back-face strain technique [189].
Figure 2-51. Variation in compressive back-face strain at constant $K = 20 \text{ MPa} \, m^{1/2}$ with $a/W$ for a 1-T Type modified WOL specimen [189].
technique which is sensitive enough to measure the crack growth rate needs to be developed.
Chapter III
EXPERIMENTAL DETAIL

3.1 Introduction

The major focus of the experimental work is on the study of the crack growth rates for intergranular stress corrosion cracking (IGSCC) of austenitic stainless steels in simulated boiling water reactor (BWR) environments as a function of applied potentials. A secondary part effort of this research is the development of an effective device to measure in-situ crack growth rate of the modified WOL specimen in that environment.

This chapter is divided into the following major sections:

1) Materials and specimen preparation: Listing of the composition, heat treatment procedures and specimen preparation procedures.

2) Testing apparatus: Description of the various pieces of equipment that were used in the course of the study.

3) Experimental procedures: This procedure section is divided into three parts. The first part describes the testing environments, procedures, and techniques used to investigate IGSCC in a simulated BWR environment. The second part describes the procedures that were used to test and
calibrate instrumented loading devices. Finally, experimental procedures for several specific experiments are illustrated.

4) Data analysis: Description of the procedures that were used to calculate the crack growth rate of the specimen when using an instrumented loading devices.

3.2 Material and Specimen Preparation

3.2.1 Chemistry and Specimen Geometry

Two heats of Type 304 stainless steel were used for this study. Table 3-1 shows the certified chemical composition and mechanical properties of these materials. Heat A was purchased directly from the manufacturer to machine the unwelded or "regular" specimen. Heat B material was donated by the Babcock & Wilcox Corporation of Barberton, Ohio, and was welded by them. This material was used to machine the welded specimen.

Type 1-T, 2.54cm (1 in) thick, Modified WOL specimens were chosen to investigate the crack growth rates. Details of the specimen geometry are shown in Figure 3-1.

3.2.2 Heat Treatment and Specimen Preparation

3.2.2.1 Regular Specimen

During the course of the study, after an initial solution annealing at 1050 °C for one hour followed by water quenching, the Heat A material was heat-treated at 650 °C for 10 and 24 hours. The modified WOL specimens were then
machined from the heat-treated specimen block according to the diagram in Figure 3-1. Since Type 304 stainless steel has good ductility, the machined notch was sometimes not sharp enough to initiate a fatigue pre-crack. Therefore, a wire type electric discharge machine (EDM) was used for sharpening the notch to approximately 0.1 mm radius by using a 34 gage copper wire (0.16 mm dia.). The specimens, fatigue pre-cracking procedure then generally followed the ASTM recommended practice E-399 [190]. They were initially loaded cyclically at between 2kN (450 lbf) and 20 kN (4,500 lbf) in an MTS machine. When extended to about 50 microns, the maximum load was reduced to 16.9 kN (3,800 lbf) to ensure that the stress intensity factor \( K_I \) at the crack tip remained smaller than 65% of the \( K_{IC} \) value of this material. A frequency of 10 Hz was used. The final fatigue pre-crack length was about 80 to 120 microns. The steps adopted for preparing the specimen for SCC testing are schematically shown in Figure 3-2.

3.2.2.2 Welded Specimen

The certified chemical composition and mechanical properties of the base and the filler metal are shown in Table 3-1. Figure 3-3 shows schematically the dimension of the welded block, weld joint structure, and the locations from which the welded modified WOL specimens were machined. In addition, Table 3-2 lists the welding procedure of this welded plate. Basically, welding procedure follows the AWS
Figure 3-1 Specification of the modified WOL specimen.
Table 3-1

Chemical Composition (wt %) and Mechanical Properties of Material Used in This Study

<table>
<thead>
<tr>
<th>Heat</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
<th>Co</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.057</td>
<td>0.49</td>
<td>1.87</td>
<td>0.024</td>
<td>0.005</td>
<td>18.80</td>
<td>8.50</td>
<td>0.43</td>
<td>0.23</td>
<td>0.14</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>0.055</td>
<td>0.66</td>
<td>1.76</td>
<td>0.022</td>
<td>0.01</td>
<td>18.50</td>
<td>8.24</td>
<td>0.29</td>
<td>0.17</td>
<td>0.72</td>
<td>0.072</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Heat</th>
<th>Tensile Strength (ksi)</th>
<th>Tensile Strength (MPa)</th>
<th>0.2% Yield Strength (ksi)</th>
<th>0.2% Yield Strength (MPa)</th>
<th>Elongation (%)</th>
<th>Reduction of Area (%)</th>
<th>Hardness (BHN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>88.5</td>
<td>610</td>
<td>46.3</td>
<td>319</td>
<td>65.0</td>
<td>75.0</td>
<td>163</td>
</tr>
<tr>
<td>B</td>
<td>91.7</td>
<td>632</td>
<td>37.6</td>
<td>259</td>
<td>58.0</td>
<td>67.0</td>
<td>156</td>
</tr>
</tbody>
</table>
Figure 3-2 Preparation steps for modified WOL specimens.

1. Flat Bar 1" ( Thickness ) x 3" ( Width )
2. Cut into Specimen Blocks, Measuring 3.5" ( Long ) x 2.7" ( Wide )
3. Annealed at 1050°C for 1 hr. Then Water Quenched
4. Sensitized at 650°C for 10 hrs. or 24 hrs. Type 304 S.S.
5. Machined to Final Size of Modified WOL Specimen
6. Sharp Crack Tip Identical with a Wire Type EDM, Wire Gage 34 ( 0.0063" )
7. Fatigue Crack Specimen by MTS Machine. Final Length of Fatigue Crack is About 80 ~ 120 μ.
Figure 3-3 Location of the WOL specimen prepared from the 2.54 cm (1") thick welded plate.
Table 3-2
Welding Procedure of Welded Block

<table>
<thead>
<tr>
<th>Welding Process:</th>
<th>GTAW and Shielded Metal Arc. Multiple Passes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Backing Strip:</td>
<td>No Backing Strip</td>
</tr>
<tr>
<td>Material:</td>
<td>Base Metal: Type 304 SS 1&quot; Thick Plate</td>
</tr>
<tr>
<td></td>
<td>Filler Metal: 1/8&quot; x 14&quot; E-308-16 Electrode Rod</td>
</tr>
<tr>
<td>Weld Characteristics:</td>
<td>GTAE Straight Polarity 15 Volt 125-160 Amps</td>
</tr>
<tr>
<td></td>
<td>Shielded Metal Arc Weld 21-23 Volt 90-110 Amps</td>
</tr>
<tr>
<td>Gas Flow Rate:</td>
<td>20 CFH/Cup Size 5/16&quot;</td>
</tr>
<tr>
<td>Position of Plate:</td>
<td>Horizontal</td>
</tr>
<tr>
<td>Size of Electrode:</td>
<td>3/32&quot; Dia. Tung/Thor. 2%</td>
</tr>
<tr>
<td>Inert Gas Commo.:</td>
<td>Argon</td>
</tr>
<tr>
<td>Cup Distance:</td>
<td>3/8&quot; to Work</td>
</tr>
<tr>
<td>Travel Speed:</td>
<td>Not Applicable</td>
</tr>
</tbody>
</table>
specification for nuclear power plants [191].

The heat treatment conditions of these specimens are listed in Table 3-3. (Note: the furnaced sensitized specimen was machined from the base metal.) The crack tip and the side groove for the specimens (including weld deposited metal) were located at a region most sensitive to intergranular attack - the heat affected zone (HAZ) near the deposited metal. An electrochemical method was used to measure the degree of sensitization (DOS) of the weld metal, base metal and HAZ. The details of this method will be mentioned in Section 3.4.4.

3.3 Testing Apparatus

3.3.1 High Temperature Circulating Autoclave System

The tests to measure the crack growth rate of the modified WOL specimen were conducted in a high temperature circulating autoclave system. This system was designed to conduct multi-specimen testing and included facilities for controlling the potential applied to each specimen and for monitoring the pH value of the solution at room temperature. A diagram of the entire system is presented in Figure 3-4, and Figure 3-5 gives an overview of the system. The various components of the system are discussed in detail in the follow sub-sections.

3.3.1.1 Solution Preparation Units

High purity water mixed with a small amount of sodium sulfate (0.01 m) was selected as the testing solution. The
<table>
<thead>
<tr>
<th></th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-1</td>
<td>Furnace sensitized at 650°C for 24 hr</td>
</tr>
<tr>
<td>W-2</td>
<td>As welded</td>
</tr>
<tr>
<td>W-3</td>
<td>Welded and heat treated at 550°C for 24 hr</td>
</tr>
</tbody>
</table>
Figure 3-4 Diagram of the circulating autoclave system.
Figure 3-5  An overview of the recirculating autoclave system.
addition of sodium sulfate was to improve the conductivity of
the solution for controlling the potential of the specimens.
Water and a suitable amount of sodium sulfate powder was
mixed with a stirrer in a 110 lit. polyester solution mixing
tank. It was then transferred to another 110 lit. polyester
solution storage tank for pre-degassing. Finally, the solu­
tion was fully degassed in a 55 lit. Type 304 stainless steel
degassing tank. The solution storage tank and degassing tank
were continuously deoxygenated with pre-purified nitrogen
gas.

3.3.1.2 Pressure Control Units

A high pressure metering pump, accumulator, pressure
gage and back pressure regulator were the four major units
used to regulate the pressure of the system. A Milroyal B
pulsating diaphragm-type metering pump with a 38 lit./hr.
maximum pumping capacity was used to pressurize the solution
from the degassing tank into the autoclave. Teflon was used
as a diaphragm in the pump; all other parts of the pump with
which the solution came in contact were made of Type 316
stainless steel. An accumulator connected between the pump
and the autoclave was employed for damping the pressure
fluctuation. Finally, at the outlet of the system, a back
pressure regulator was installed. This device allows for the
adjustment of the operating pressure of the system, which
could be read by a pressure gage connected to the autoclave.
3.3.1.3 Autoclave

A 20 lit. autoclave (21.6 cm ID, 48 cm long) was designed and constructed for this study in order to conduct multi-specimen tests. Six modified WOL specimens could be tested simultaneously. A detailed diagram of the autoclave is shown in Figures 3-6 and 3-7. Figure 3-8 shows the outlook of the autoclave.

The cylindrical body of the autoclave was made of a centrifugally cast stainless steel pipe (Type CF 8M stainless steel with a composition equivalent to that of Type 316 stainless steel). The alloy composition, the manufacturing after casting, and details of the inspection requirements for pressure vessel materials according to ASTM A351 specifications [192] are presented in Table 3-4. The closure of the autoclave at both ends was accomplished by the use of heavy clamps made of Type 410 stainless steel and Teflon gaskets which act as seals. The details of the materials and dimensions of the autoclave components are shown in Table 3-5.

3.3.1.4 Temperature Controlling Units

The autoclave was heated by three internal stainless steel-cladd heaters (240 Volts, 1000 Watts), and it was covered by a thick insulation jacket (two-inch thick fiberglass) to avoid heat loss to the surrounding environment. Before the solution was transferred to the autoclave, it passed through a set of heat exchanging pipes (totalling about 7 meter) and an 3-meter long pre-heating pipe heated
Figure 3-6 Schematic of autoclave assembly.
Figure 3-7 Schematic of (a) top lid and (b) bottom lid of the autoclave.
Figure 3-8 The multi-specimen autoclave.
Table 3-4

Composition, Manufacturing Procedure, and Inspection Requirements for the Autoclave Material

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat No.</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM A351 CF8M</td>
<td>5217</td>
<td>0.06</td>
<td>1.21</td>
<td>1.13</td>
<td>0.022</td>
<td>0.024</td>
<td>20.37</td>
<td>10.19</td>
<td>2.12</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Manufacturing and Inspection Techniques:

(1) Centrifugally cast alloy was heat treated and rough machined to OD 11.00 in x ID 8 1/4 in x length 20.00 in with square cut ends.

(2) After the rough machining, all surfaces were inspected by liquid penetration according to ASME Sec. VIII.

(3) Finally, radiographic examination was performed according to ASME Sec. VIII.
<table>
<thead>
<tr>
<th>ITEM</th>
<th>MATERIAL</th>
<th>DIMENSION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top Lid</td>
<td>316 Stainless Steel</td>
<td>10.75&quot; dia., 3&quot; T</td>
</tr>
<tr>
<td>Bottom Lid</td>
<td>316 Stainless Steel</td>
<td>10.75&quot; dia., 25&quot; T</td>
</tr>
<tr>
<td>Vessel Body</td>
<td>CF-8M</td>
<td>8.5&quot; I.D., 10.75&quot; O.D., 19&quot;L</td>
</tr>
<tr>
<td>Top Clamp</td>
<td>410 Stainless Steel</td>
<td>8.0&quot; I.D., 12.75&quot; O.D., 5&quot;L</td>
</tr>
<tr>
<td>Bottom Clamp</td>
<td>410 Stainless Steel</td>
<td>8.0&quot; I.D., 12.75&quot; O.D., 4.5&quot;L</td>
</tr>
<tr>
<td>Pushing Ring</td>
<td>CF-8M</td>
<td>8.5&quot; I.D., 10.75&quot; O.D., 1/4&quot;T</td>
</tr>
<tr>
<td>Sealing Gasket</td>
<td>PTFE</td>
<td>8.5&quot; I.D., 9.25&quot; O.D., 1/32&quot;T</td>
</tr>
<tr>
<td>Top Coupling</td>
<td>4140 Carbon Steel</td>
<td>12.75&quot; I.D., 13.35&quot; O.D., 5&quot;L</td>
</tr>
<tr>
<td>Bottom Coupling</td>
<td>4140 Carbon Steel</td>
<td>12.75&quot; I.D., 13.35&quot; O.D., 4.5&quot;L</td>
</tr>
<tr>
<td>Bolts (26)</td>
<td>4140 Carbon Steel</td>
<td>7/8&quot; dia., 1 1/2&quot;L, Regular Threaded</td>
</tr>
</tbody>
</table>
by two 200 watt flexible electric heating tapes, so that it could recover part of the heat from the solution leaving the autoclave and gain a temperature close to the temperature of the autoclave.

Type K thermocouples were used to monitor the temperature of the autoclave and the pre-heating pipe, and two on-off type temperature controllers were used to control the temperature of these two units. The electrical wiring diagram for the temperature control units is shown in Figure 3-9.

3.3.1.5 pH Measurement

Two S200C STD Sensores pH electrodes and flow cells were installed in the circulating autoclave system to monitor the pH values of the solution at the inlet and outlet of the system during testing. Owing to their unbreakable polymer bodies and sealed reference design, these electrodes can operate for long periods and eliminate the need to replenish the filling solution during testing. On the other hand, owing to the extremely high internal resistance of this type of electrode (of the order of gigaohms), a specially designed voltage follower, shown in Figure 3-10, was used for matching the output impedance of the electrode to the input impedance of the data acquisition system.

3.3.1.6 Emergency Cut-off System

The emergency cut-off system utilizes through a dual needle contact-face mounted on the pressure gauge. When the
Figure 3-9 Electrical wiring diagram for temperature control and emergency cut-off systems.
Figure 3-10 A simplified diagram for voltage follower to match the impedance between the pH electrode and the recorder.
pressure is higher or lower than the values set by those needles, the contact-face sends the appropriate signal for turning off both the power of the heaters and the pumps to eliminate the danger of explosion or excessive leakage. The wiring diagram of this emergency system is also shown in Figure 3-9.

3.3.2 Specimen holder

A specimen holder was specially designed to hold and support six sets of specimens, load cells, and counter electrodes inside the autoclave. Figure 3-11 shows an overview of the specimen holder with and without specimens. A diagram of one specimen holding unit of the holder is shown in Figure 3-12. The counter electrodes were made of Type 304 stainless steel sheets. PTFE bolts, sheets, and washers were used to insulate the specimens from the counter electrodes and the specimen holder. Hence, each specimen could be tested under different applied potentials at the same time.

3.3.3 Load Monitoring Devices

Three types of loading devices, compression load cell (LC), external instrument bolt (EIB), and internal instrument bolt (IIB), have been studied in order to monitor in-situ the load variation of the modified WOL specimen during testing. All of these loading devices are excited by a 10-Volt DC stabilized power supply, as seen in Figure 3-13. Table 3-6 summarizes the basic design criteria of these loading devices. The following sections describe them in more
Figure 3-11 View of the specimen holder with and without specimens.
Figure 3-12 Schematic of specimen and specimen holding unit.
Figure 3-13 Wiring diagram of the 6-channel DC stabilized power supply.
Table 3-6
Design Criteria for Instrumented Loading Devices

<table>
<thead>
<tr>
<th>Type</th>
<th>Strain Gauge Type</th>
<th>Material</th>
<th>Strain Gauge Configuration</th>
<th>Capacity kN</th>
<th>Excitation voltage (V)</th>
<th>Operating temperature Range(°C)</th>
<th>Sensitivity range (kN/mV)</th>
<th>Basic Design Criteria</th>
<th>Sealing Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compression load cell (LC)</td>
<td>High temp. Ni-Cr foil strain gauge</td>
<td>17-4 PH</td>
<td>2 active and 2 dummy strain gauges form a full bridge circuit</td>
<td>0-26.7</td>
<td>10</td>
<td>15-350</td>
<td>0.76-1.3</td>
<td>4 strain gauges are mounted on the load frame located inside the load cell. They measure the tensile strain on the frame as the load stud transmits the load to the load frame.</td>
<td>Load cell chamber is welded by a no-filler metal tungsten inert gas welding process.</td>
</tr>
<tr>
<td>External Instrumented Bolt (EIB)</td>
<td>Alltech MG 125 Ni-Cr weldable strain gauge</td>
<td>Inconel X-750</td>
<td>2 active strain gauges form a half bridge circuit</td>
<td>0-26.7</td>
<td>10</td>
<td>-200-350</td>
<td>20-2.2</td>
<td>2 strain gauges are welded on the side surface of the bolt case. They measure the tensile strain variation when load stud transmits load to end of bolt case.</td>
<td>Strain gauge is self-sealed in an AISI Type 321 SS sheath.</td>
</tr>
<tr>
<td>Internal Instrumented Bolt (IIB)</td>
<td>Alltech MG 425 Pt-W weldable strain gauge</td>
<td>Inconel X-750</td>
<td>1 active and 1 dummy strain gauge form a half bridge circuit</td>
<td>0-26.7</td>
<td>10</td>
<td>-200-600</td>
<td>1.2-1.3</td>
<td>1 strain gauge is imbedded in the load stud by silver brazing. It measures the compression strain variation as the load stud is compressed by the load.</td>
<td>Strain gauge is self-sealed in an AISI Type 321 SS sheath.</td>
</tr>
</tbody>
</table>
3.3.3.1 Compression Load Cell

Each compression load cell consists of a load cell chamber, a load stud, and a loading bolt designed for the modified WOL specimen (see Figures 3-14 and 15). All these elements were made of Type 17-4 precipitate hardening (17-4 PH) stainless steel. The elements were machined in the annealed condition of the material, and were hardened at 482 °C for 1 hour to obtain a yield strength of 1241 Mpa (180 ksi) after hardening. A high temperature full bridge strain gage circuit and a temperature compensation unit were sealed inside the load cell chamber using a no-filler metal tungsten inert gas welding process to avoid leakage of water at 288 °C under 6.9 MPa (1,000 psi). Figure 3-16 shows the compression load cell attached to the specimen through the loading bolt. All load cells were calibrated by the manufacturer. Table 3-7 presents a set of typical calibration data. The lead wires of the load cell were made of magnesium oxide insulated cable sheathed with a 0.24 cm (3/32 inch) Type 304 stainless steel tube.

3.3.3.2 External Instrumented Bolt

Figures 3-17 and 18 show the design drawing and an overview of the EIB. The bolt consists of two major components, a load cell case and load stud, both made of Inconel alloy X-750. Inconel alloy X-750 was chosen because it has good corrosion and oxidation resistance and a
NOTE TEMPORARY COLOR CODED LEAD WIRES FINAL TO BE DONE BY THE CUSTOMER.

TEMPORARY COLOR CODE:
- RED - EXCITATION
- BLACK - EXCITATION
- WHITE - OUTPUT
- GREEN - OUTPUT

Figure 3-14 Design drawing of modified compression load cell.
Figure 3-15 An overview of the compression type load cell assembly.
Figure 3-16 Assembled view of compression type load cell and specimen.
Table 3-7

Calibration Record of Load Cells

Type: Compression
Model No.: 1876
Capacity: 0 ~ 6000 lbs.

Excitation Volts: 10 volts DC
Compensated Temperature Range: 60°F ~ 600°F
Manufacturer: Sensotec Inc.

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>0% 'capacity</th>
<th>50% capacity</th>
<th>100% 'capacity</th>
<th>Decending (mV) 50% capacity</th>
<th>Resistance (Ω)</th>
<th>Shunt Resistor Value of 59 KΩ Across Green and Black Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>63117</td>
<td>0</td>
<td>10.122</td>
<td>20.375</td>
<td>10.285</td>
<td>531.0</td>
<td>354.0</td>
</tr>
<tr>
<td>63118</td>
<td>0</td>
<td>10.204</td>
<td>20.249</td>
<td>10.212</td>
<td>556.0</td>
<td>356.0</td>
</tr>
<tr>
<td>63119</td>
<td>0</td>
<td>9.788</td>
<td>19.680</td>
<td>9.899</td>
<td>590.0</td>
<td>354.0</td>
</tr>
<tr>
<td>63120</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>63121</td>
<td>0</td>
<td>10.025</td>
<td>20.061</td>
<td>10.113</td>
<td>553.0</td>
<td>354.0</td>
</tr>
<tr>
<td>63122</td>
<td>0</td>
<td>9.969</td>
<td>19.977</td>
<td>10.068</td>
<td>512.0</td>
<td>354.0</td>
</tr>
<tr>
<td>63123</td>
<td>0</td>
<td>10.053</td>
<td>20.100</td>
<td>10.104</td>
<td>499.0</td>
<td>352.0</td>
</tr>
</tbody>
</table>
Figure 3-17 Design drawing of the external instrumented bolt (EIB).
Figure 3-18 An overview of the EIB. (A) Instrumented loading bolt assembly; a) Bolt Case; b) Loading Stud; c) Bearing ball for centering the load; and d) Potting Boot. (B) EIB and specimen.
high creep-rupture strength up to 800 C [193]. The bolts were machined under a hot-finished condition. In order to obtain a stable high temperature creep resistance, they then went through a two-stage heat treatment. First of all they were heated at 885 C for 24 hours, and then air-cooled. They were then heated at 700 C for 20 hours, and again were air-cooled. The physical constants and thermal properties, as well as the room temperature mechanical properties, of this material are shown in Table 3-8.

Two Altech MG 125 weldable strain gages, sheltered in a Type 321 stainless steel capsule, were welded on the outer surface of each cell case using low energy capacitive discharge spot welding equipment. These gages were made of a Ni-Cr alloy and had a gage factor of about 2. They were connected as a half bridge circuit which senses the load variation through the strain variation on the wall of the bolt case. The lead wires of the weldable strain gages were made of copper conductors insulated with magnesium oxide and encased in a 0.16 cm (1/16 inch) Type 347 stainless steel tube. These lead wires were very fine (gage 30 copper wires) and fragile. A potting boot with an 18 inch flexible lead wire was connected to the end of the stainless tube lead wire to facilitate operation (see Figure 3-18). Table 3-9 lists the specification and the design criteria of the EIB.
Table 3-8
Physical Properties of Inconel X-750 Alloy

<table>
<thead>
<tr>
<th>Property</th>
<th>Room Temp.</th>
<th>250°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's Modulus $10^6$ PSI</td>
<td>31.0</td>
<td>28.7</td>
</tr>
<tr>
<td>Mean Linear Expansion in/in/in/$^\circ$F x 10$^{-6}$</td>
<td>0</td>
<td>7.3</td>
</tr>
<tr>
<td>Yield Strength (ksi) After Equalized and Precipitation—Treated ($1625^\circ$F/24 hr. + $1300^\circ$F/20 hr.)</td>
<td>119</td>
<td>109</td>
</tr>
</tbody>
</table>
Table 3-9

Specification and Design Criteria of EIB

**Specification**

Bolt Design: See Figure 3-17

Bolt Material: Inconel X-750 (70 Ni - 14 Cr - 5 Fe - 3 Ti - 0.5 Al)

Gage No.: MG 125

Operating Temperature: 70°F - 500°F

Lead Wire: Three No. 30 AWG bare copper wire insulated with compacted MgO, encased in Type 347 Stainless Steel tube.

**Design Criteria**

Maximum Design Load: 6000 lbs.

Stress at Max. Load: at load stud: 54.4 KSI

at treading region: 51 KSI

Maximum Strain Detected by Attached Strain Gages at the Max. Load:

\[ \Delta \varepsilon_1 + \Delta \varepsilon_2 = 1600 \mu \varepsilon \]
A two-channel half-bridge circuit was built for the EIB for readings to be taken by a data acquisition system. Because one EIB contains only two active strain gages, it is necessary to connect two dummy resistors to form the Wheatstone bridge circuit. Figure 3-19 shows the arrangement of the bridge circuit and the design diagram of this 2-channel half bridge circuit. When this circuit is well balanced, the equation of the output signal, \( E_o \), of the EIB for this circuit can be simplified as follows [194]:

\[
E_o = \frac{E_{in}}{4} \times G.F. \times (\varepsilon_1 + \varepsilon_2) \quad \text{Eqn. 3-1}
\]

where:

- \( E_o \) = Output signal
- \( E_{in} \) = Excitation voltage
- G.F. = Gage factor (1.7 for MG 125 weldable strain gage)
- \( \varepsilon_1 \) = Strain of the No. 1 strain gage
- \( \varepsilon_2 \) = Strain of the No. 2 strain gage

According to this circuit, the load-signal of the EIB is about 7 mV when it loaded up to 26.7 kN (6000 lbf.)

3.3.3.3 Internal Instrumented Bolt

Figures 3-20 and 21 show the design drawing and an overview of the IIB and the regular loading bolt. Table 3-10 lists the specification and design criteria of the IIB. This type of instrumented bolt was made of the same material as the EIB, i.e. Inconel alloy X-750. It was
Figure 3-19  A) Wiring diagram of EIB and dummy resistors.  
B) Design diagram of the 2-channel half-bridge circuit for EIB.
Figure 3-20 Design drawing of the internal instrumented bolt gage. (IIB)
Figure 3-21 An overview of the IIB (the lower one) and the regular bolt (the upper one).
Table 3-10
Specification and Design Criteria of IIB

### Specification

**Bolt Design:** See Figure 3-20

**Bolt Material:** Inconel X-750 (70 Ni - 14 Cr - 5 Fe - 3 Ti - 0.5 Al)

**Gage No.:** SG 425

**Operating Temperature:** 70°F - 600°F

**Lead Wire:** Three No. 30 AWG bare copper wire insulated with compacted MgO, encased in Inconel 600 Alloy tube.

### Design Criteria

**Maximum Design Load:** 6000 lbs.

**Maximum Stress (at Max. Load):**
- at load stud: 68 KSI
- at threaded region: 33 KSI

**Maximum Strain Detect by Embedded Strain Gage (at Max. Load):**
\[
\Delta E = 2200 \mu e
\]
machined under at a hot-finished condition to the shape of the regular loading bolt. It then underwent the double stage heat treatment process mentioned in the last section. A 0.14 cm by 0.10 cm elliptical hole was machined by EDM through the center of the bolt and extending about 5 cm from the top of the bolt. Another EDM cut, an annular ring with 0.064 cm width and 0.95 cm internal diameter, was made from the bottom of the bolt and extending up about 3.8 cm. Finally, an Ailtech SG 425 strain gage was embedded inside the hole by silver brazing.

The Ailtech SG 425 strain gage is made of Platinum-Tungsten alloy filaments which are suitable for static and dynamic strain measurements up to 650°C. They offer optimum temperature and nuclear radiation resistance. In addition, the gage is a half-bridge instrument utilizing an active and a true dummy element within a single strain tube (Figure 3-22) [195], so that the exact temperature compensation can be achieved using an external fixed, or "ballast", resistor placed in the bridge completion network. Table 3-11 shows detailed specifications of this gage. It should be noted that the gage factor is about 4, which is twice the value of that for MG125. For a balanced bridge circuit, the load-signal of IIB is as follows [194]:

$$E_o = E_{in}/4 \times G.F. \times \epsilon$$

Eqn. 3-2

where $E_o$, $E_{in}$, G.F., and $\epsilon$ are the same as parameters
Figure 3-22 The schematic of bridge completion network of Altech 425 weldable strain gage.
Table 3-11
Specifications of Altech 425 Series Weldable Strain Gage

**ELECTRICAL SPECIFICATIONS**

<table>
<thead>
<tr>
<th>Strain Gage Resistance</th>
<th>Model: SG 425</th>
<th>MG 425</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistance</td>
<td>115 ohms ± 10</td>
<td>115 ohms ± 10</td>
</tr>
<tr>
<td>Resistance Match</td>
<td>Active / Dummy</td>
<td>8 ohms</td>
</tr>
</tbody>
</table>

**Integral Lead Wire Resistance**
0.1 ohms / ft. at 75°F.

**Excitation Current**
Continuous: 50 ma maximum
Pulsed: To 300 ma depending on operating temperature and test structure.

**Insulation Resistance**
Greater than 1000 Megohms at 50 vdc measured at 75°F.
10 meghoms at 1200°F.

**PERFORMANCE SPECIFICATIONS**

**Gage Factor**
Nominal value 4.2. SG 425 4.0, MG 425 3.5; The effective gage factor varies with required compensation resistance and is reported with each gage.
The actual gage factor for all gages within a particular lot is within ± 3% for SG 425 gages and 5% for MG 425 gages.

**Rated Strain Level:**
≤ 6,000 microinches per inch

**Fatigue Life:**
Exceeds 10⁶ cycles at ≤ 1,000 microinches per inch

**Transverse Sensitivity:**
Negligible (Line weld between strain tube and mounting flange)

**ENVIRONMENTAL SPECIFICATIONS**

**Operable Temperature Range**
Static and dynamic measurements –452 to 1200°F.

**Compensated Temperature Range**
Gages are individually temperature compensated

<table>
<thead>
<tr>
<th>Designation</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>–01</td>
<td>75 to 600°F.</td>
</tr>
<tr>
<td>–08</td>
<td>75 to 900°F.</td>
</tr>
<tr>
<td>–09</td>
<td>Special Range</td>
</tr>
</tbody>
</table>

(Specify on order)

**Caution:** If the temperature of the strain gage exceeds 1200°F, the gage may be permanently damaged.

**Humidity:** 100% at 180°F – 100 PSI at 80°F.

**Apparent Strain vs. Temperature**
With the proper compensating resistor (Rtc) at the readout equipment, the apparent strain at the maximum temperature of the compensated range is less than 250 microstrain.
Typical values are 0.12 microstrain. The bow or maximum deviation due to temperature from a straight line output occurs midway in the compensated temperature range and is reported for each gage. Typical bow values are ~350 microstrain.

**Compensating Resistors**
Temperature compensating resistor (Rtc) — SG 070.
Circuit balance resistor (Rbal) — MG 071.

**ORDERING INFORMATION**
Detailed ordering information and available options are shown on a separate instruction sheet.

**Standard Gages**
Standard Gages are stocked in limited quantities for immediate shipment. These gages solve the majority of strain measurement problems encountered. They include ten feet of integral cable, and are compensated to match 1018 steel (6S) or 321 stainless steel (9S) over the temperature range of 75 to 900°F.

**Custom Gages**
Ordering of Custom Gages with other cable lengths, other temperature ranges, options, compensations etc., requires a detailed build-up of the Custom model number.

**Compensation Resistors**
Temperature compensating resistor (Rtc) — SG 070.
Circuit balance resistor (Rbal) — MG 071.
Consult factory for further information or applications assistance.

**Linear Sinusoidal Vibration:** 35g. 20 to 2000 cps
**Static Acceleration:** 50g
**Shock:** 100g half sine, 7 millisecond duration
**Acoustic noise:** 150 db.
**Ambient Pressure:** Vacuum to 10,000 psi.

**Nuclear Radiation:**
The strain gage contains no organic material.
defined previously. The estimated load-signal under the maximum load (27.6 KN) is approximately 24 mV.

Finally, Figure 3-23 shows the gage's cumulative drift microstrain as a function of the temperature and time for SG425 and SG125 strain gage. It indicates that the signal drift of the IIB at the SCC testing temperature, 250 °C (482 °F), should be negligible.

3.3.4 Other Devices for Conducting the SCC Tests

Except for the loading devices and stabilized DC power supply, three units were used to monitor load relaxation during crack growth and to control the potential applied separately to each specimen. These were a potentiostat, a data acquisition system, and a reference electrode. Figure 3-23 is a schematic illustration of the experimental set-up. The details and function of each unit are described below.

3.3.4.1 Potentiostat

Six potentiostats (4 Wenking LT73, maximum current 0.1A, and 2 Wenking LT72, maximum current 1A) were employed. These potentiostats were operated at a virtual ground state allowing the potential applied to each specimen to be controlled individually. The use of a six-channel potentiostat has unsuccessful because each channel had a common ground so that the potential of each specimen could not be controlled individually.
Figure 3-23 The variation of strain gages, cumulative drift microstrain as function of time and temperature.
Figure 3-24 Schematic drawing of the set-up for load monitoring and potential control units.
3.3.4.2 **Data Acquisition System**

An Esterline Angus Model PD2064 programmable data acquisition system was used in this study. The system has 24 channels for the acquisition of voltage signals in the range from 0.001 mV to 4 V. Because the built-in ROM stored a set of thermocouple linearization functions, the data acquisition system could monitor the temperature directly from Type K and Type F thermocouples. Table 3-12 gives a list of the typical functions assigned to each channel of the system for a SCC test operated inside the autoclave.

3.3.4.3 **External Reference Electrode**

External pressure balanced Ag/AgCl (0.1m KCL) reference electrodes were used for controlling and measuring the potential of the specimens. Figures 3-25 and 26 are a schematic diagram and an overview of the external Ag/AgCl reference electrodes. A silver chloride coating was electro plated on the silver electrode in 1 N HCl solution for 24 hours, and the applied current was controlled at 3 mA for each electrode. The coated Ag/AgCl electrode was sealed in a Type 316 stainless steel compartment. The compartment contained a 0.1m KCl solution in electrolytic contact with the external solution through a zirconia oxide liquid junction. All potentials measured using the external Ag/AgCl reference electrode were converted to the standard hydrogen electrode (SHE) by using appropriate data [196]. Figure 3-27 shows the calibration curve of the external Ag/AgCl/0.1m KCl ref-
### Table 3-12

Functions Assigned to Each Channel of the Data Acquisition System

<table>
<thead>
<tr>
<th>Channel</th>
<th>Assigned Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Temperature at top of autoclave</td>
</tr>
<tr>
<td>1</td>
<td>Temperature at bottom of autoclave</td>
</tr>
<tr>
<td>2</td>
<td>pH value</td>
</tr>
<tr>
<td>3</td>
<td>pH value</td>
</tr>
<tr>
<td>4</td>
<td>Excitation voltage of signal condition</td>
</tr>
<tr>
<td>5</td>
<td>Excitation voltage of signal condition:</td>
</tr>
<tr>
<td>6</td>
<td>Load of specimen No. 1</td>
</tr>
<tr>
<td>7</td>
<td>Load of specimen No. 2</td>
</tr>
<tr>
<td>8</td>
<td>Load of specimen No. 3</td>
</tr>
<tr>
<td>9</td>
<td>Load of specimen No. 4</td>
</tr>
<tr>
<td>10</td>
<td>Load of specimen No. 5</td>
</tr>
<tr>
<td>11</td>
<td>Load of specimen No. 6</td>
</tr>
<tr>
<td>12</td>
<td>Corrosion current of specimen No. 1</td>
</tr>
<tr>
<td>13</td>
<td>Corrosion current of specimen No. 2</td>
</tr>
<tr>
<td>14</td>
<td>Corrosion current of specimen No. 3</td>
</tr>
<tr>
<td>15</td>
<td>Corrosion current of specimen No. 4</td>
</tr>
<tr>
<td>16</td>
<td>Corrosion current of specimen No. 5</td>
</tr>
<tr>
<td>17</td>
<td>Corrosion current of specimen No. 6</td>
</tr>
<tr>
<td>18</td>
<td>Applied potential of specimen No. 1</td>
</tr>
<tr>
<td>19</td>
<td>Applied potential of specimen No. 2</td>
</tr>
<tr>
<td>20</td>
<td>Applied potential of specimen No. 3</td>
</tr>
<tr>
<td>21</td>
<td>Applied potential of specimen No. 4</td>
</tr>
<tr>
<td>22</td>
<td>Applied potential of specimen No. 5</td>
</tr>
<tr>
<td>23</td>
<td>Applied potential of specimen No. 6</td>
</tr>
</tbody>
</table>
Figure 3-25 Schematic of external reference electrode assembly.
Figure 3-26 The outlook of external Ag/AgCl reference electrodes.
Figure 3-27 The calibration curve of the pressure balanced external Ag/AgCl/0.1m KCl electrode. [37]
erence electrode. It indicates that, at 250 °C, the SHE reading is the electrode reading plus 0.022 V.

3.4 Testings Procedures

3.4.1 Pre-testing of the Circulating Autoclave System

In order to develop a compact oxide film on the inner surface of the autoclave, the circulating system was pre-tested at 178 °C under a pressure of 34 atm (500 psi) for two weeks. The testing solution was aerated 0.01M sodium sulfate. The heating and pumping units performed satisfactorily and no leakage was observed during the entire testing period. The maximum difference in temperature between the top and the bottom of the autoclave, with and without stirring, was approximately 0.4 and 1 °C, respectively. This temperature difference was considered to be negligible and indicates that the combination of internal heaters and good insulation of the autoclave walls provides excellent temperature control. Therefore, the use of the magnetic stirrer became unnecessary for the further testings.

3.4.2 SCC Testing in Autoclave

3.4.2.1 Specimen Loading and Installation

After fatigue pre-cracking, specimens were degreased with acetone in an ultrasonic cleaner for about 10 minutes and then loaded either by instrumented loading devices or by regular loading bolts (Figure 3-21) to initial $K_T$ values ranging from 20 to 45 MPa m$^{1/2}$. For the specimens loaded by
the instrumented loading devices, because the load of the specimen was known, the initial $K_I$ values were calculated directly by using equation 2-3. However, for those specimens loaded by regular loading bolts, the equation 2-8 was employed to calculate the initial $K_I$ values. In this case, the COD was measured by the clip gage.

In some specimens, deep side grooves were machined. For these specimens, $K_I$ values were calculated using the equation derived from Ref. 198.

$$K_{ISG} = K_I \left(\frac{B_N}{B}\right)^{1/2} \left(\frac{I_{SG}}{I}\right)^{1/6}$$

Eqn. 3-3

where:

- $K_I$ = the stress intensity for the un-grovved specimen
- $I$ = moment of initia of the beam of the smooth around its neutral axis
- $I_{SG}$ = moment of inertia of the beam of the side-grovved specimen around its neutral axis

The conventional three-electrode configuration was employed to control the potential of each specimen, as shown in Figure 3-24. Insulated specimen holders were used to support each of the six specimens and their corresponding counter electrodes, as illustrated in Figures 3-11 and 3-12. The specimens, arrangement inside the autoclave is further revealed in Figures 3-6 and 3-28. The electrical connections from the specimens and the counter electrodes to the potentiostats were achieved with PTFE-coated Inconel 600
Figure 3-28 Schematic of load cells and specimens assembly.
wires. Different types of machined PTFE seal inserts were used to insulate the lead wires of instrumented loading devices, working electrodes and reference electrodes from the autoclave body.

3.4.2.2 Experimental Operation

The solution employed in all tests was 0.01m Na$_2$SO$_4$, prepared in the mixing tank by adding analytical reagent grade sodium sulfate to high purity water (conductivity < 100 nS/cm). The addition of the electrolyte was to improve the conductivity of the testing solution, and it has been suggested that the sulfate anion does not have an inhibiting or accelerating effect on the SCC behavior with respect to pure water. [143] Before initiating an experiment, the solution was deoxygenated with pre-purified N$_2$ for 10 hours to obtain an oxygen concentration lower than 20 ppb.

Once the oxygen concentration level was reached, the diaphragm pump was then activated, and the pressure was set to 68 atm (1000 psi.) via the back pressure regulator, and the solution drained out of the loop at flow rates of between 1.5 and 2.5 lit/hr. The system was then heated to about 90 $^\circ$C, and all the fittings were tightened again to avoid any leakage at the normal testing condition of 250 $^\circ$C/47.6 atm (700 psi). After positioning the insulating jacket, the temperature and pressure were gradually adjusted to the assigned operating condition mentioned above.
After a steady state corrosion potential was attained at approximately 100 hours, potentials ranging from $-0.3$ to $0.3 \text{ V}_{\text{SHE}}$ were applied to different specimens. Separate potentiostats, floating above ground, were used for independently controlling the potentials of each specimen. The relaxation of the load, the applied potential, and the current were monitored at 30 or 60 min intervals during the various tests that lasted from 500 to over 700 hours. Temperature was recorded, as was the pH of the inlet and outlet solutions.

### 3.4.2.3 Specimen Examination After Testing

After testing, the final load of the loading devices and the COD of the specimens were recorded. Specimens were then loaded by a MTS machine to the recorded COD value of that specimen. These MTS loading values were used to examine the performance of the loading devices and to calculate the final $K_I$ values for specimens loaded with regular loading bolts or with damaged loading devices. The side surfaces of the specimens were then machined to the full depth of the side grooves, followed by grinding and mechanical polishing, in order to measure the length and the pattern of the intergranular crack using optical microscopy. Each specimen was then broken apart by cyclic fatigue loading in air. The fracture surfaces were examined using a Scanning Electron Microscope (SEM), before and after deposited corrosion products were removed with a 50 vol% HCl solution containing 2 g/lit. of hexamethylenetetramine as an inhibitor. Because
significant crack tunnelling occurred during fatigue pre-cracking and during SCC testing, an average crack length, a, was measured on the fractographs using the simple relationship
\[ a = \frac{\sum_{i=n}^{7} a_i}{7} \]  
Eqn. 3-4
where \( a_i \) denotes the crack length at seven equally spaced positions across the fracture surface. The average crack length obtained was then divided by the exposure time under applied potential to determine an average crack growth rate. Alternatively, the maximum crack growth rate was calculated by dividing the longest IGSCC crack, observed on the fracture surface under the SEM, by the testing time. Detail of the procedures for calculating the in-situ crack growth rate of the specimen loaded with instrumented loading device will be described in Section 3.5.

3.4.3 Loading Devices

In order to understand the performance of the loading devices designed in this study, several procedures were conducted. Firstly, at room temperature, these loading devices were calibrated by a modified WOL specimen (which was pre-calibrated by a MTS machine) with a MTS clip gage (Model 632.03 b-20) (Figure 3-29). Then the shunt calibration technique [194] was used to verify the relationship between the load-signal and the actual load at the high temperature. The sensitivity and the linearity of the load-signal of the
Figure 3-29 An over-view of the set-up to calibrate the instrumented loading device.
loading devices verse the load at both the room and high temperature can be examined by these testing results. Finally, these loading devices were tested under no-load and load conditions at room temperature and at 250 °C (in a furnance) for a long period of time in order to study their stability.

After going through all these procedures, the loading devices were tested in the autoclave under the normal SCC testing condition. The durability of these loading devices against corrosion could be verified. In addition, these loading devices were also tested in an autoclave located in a by-pass steam line of a fossil-fueled power plant (Fort Martin power station, Maidsville, West Virginia), see Figure 3-30. The testing temperature and moisture content of the steam was controlled at about 150 °C and 0.2%, respectively. The load-signal of the loading devices was directly recorded by the computer system of the power station. This investigation enable us to examine the performance of these loading devices for the field test.

(Note: The modified WOL specimens for the field test were made by ASTM A470 turbine rotor steel)

3.4.4 Degree of Sensitization Study

The anodic polarization test developed by Medvedeva and co-worker [199] and our laboratory [83] was used to study the DOS of the furnace-sensitized specimens and the welded specimens. Perchloric acid solution with the addition of
Figure 3-30 An over-view of the autoclave in the field test station.
0.2 N sodium chloride was selected as the electrolyte. The DOS was evaluated by the current density at 290 mV_{SHB} of the forward polarization scan measured in that electrolyte. In addition, a sequential polishing and measurement technique [89], shown in Figure 3-31, was used to measure the DOS of the welded specimen to locate the region most sensitive to IGSCC. A conventional three-electrode electrochemical set-up was used to carry out these measurements. Figure 3-32 shows the set up of electrochemical test.

3.4.5 STEM Study

In order to study the differences in the crack growth rate of the furnace-sensitized specimen and the as-welded plus LTS sensitized specimen, a JEOL 200CX electron microscope equipped for scanning transmission electron microscopy (STEM) operation was used to examine the carbide and the chromium depletion near grain boundaries of these specimens. After a sequential cutting, grinding and polishing process, several ring shaped specimens (standard TEM specimen, about 3.0 mm in diameter and 0.01 cm in thickness) were prepared. The extra thin layer (thinner than 100 nm) of these specimens were prepared by the jet polishing machine (Tenupol made by Struers). The polishing solution was nitric acid (25% by vol.) in methanol, and the testing voltage and current were at the above applied potential, the temperature of the polishing solution was maintained between -40 to -60 °C by circulating liquid nitrogen through the cooling system of the
Figure 3-31 Schematic of the sequential-polishing technique in measuring the DOS of the HAZ of a welded structure.
Figure 3-32 Schematic of the set-up of the DOS test.
jet polishing machine.

The prepared specimens were then examined with the electron microscope in the STEM mode or the TEM mode at 200 kV to study the size, shape, and structure of the carbide precipitates located at the grain boundaries. The concentration profiles for chromium, nickel, and iron across a grain boundary were then determined by energy dispersive X-ray analyses using the STEM mode.

3.4.6 SCC in Sodium Sulfate Solution

It has been reported that sodium thiosulfate solutions induces fast crack growth rates ($\sim 10^{-6}$ m/s) in sensitized Type 304 stainless steel [200]. This solution was selected to study the effectiveness of the load relaxation method for measuring crack propagation rates. One modified WOL specimen of Type 304 stainless steel, sensitized at 650 °C for 24 hours, was loaded with IIB and tested in an aerated or 0.5 M $\text{Na}_2\text{S}_2\text{O}_3$ solution at room temperature under an applied potential of 0.15 V$_\text{SHE}$. During the test, the load, as well as the COD, of the specimen was monitored at 30 minute intervals. Figure 3-33 shows the experimental set up. The calculation of the in-situ $K_I$ value and the crack growth rate of the specimen will described in the next section.
Figure 3-33 Schematic of the set-up of the room temperature SCC test.
3.5 Analysis of the Data Obtained from Instrumented Loading Devices

The object of loading the modified WOL specimen with an instrumented loading device is to monitor the in-situ crack growth rate of the specimen during SCC tests in solution at elevated temperatures. In addition, the crack growth rate, as a function of $K_I$, can be obtained by using the fracture mechanics equations developed in the literature. Figure 3-32 outlines the procedures that show how the load signal of a loading device converts to the load, then to the $K_I$ value and crack length, and finally to the crack growth rate, as well as the relationship between the crack growth rate and $K_I$ value.

Because the excitation voltage (10 volts) of the loading devices was not very stable (it varied about 0.1 volt during the test), the load cell signal was first normalized by the exact excitation voltage recorded by the data acquisition system. The normalized data was then converted to the correct load of the specimen using the slope of the loading device calibration curve.

For a specimen loaded with a rigid instrumented loading device, which means the COD of the specimen is a constant as the load decreases during the test, the in-situ $K_I$ value of the specimen can be directly calculated by using equation 2-3. On the other hand, in order to obtain the in-situ crack length, a computer program is necessary. Accordingly, a program was written incorporating equation 3-7 which was
obtained by rearrangement of equations 2-5 and 2-7.

\[ 36.845(a/w)^4 - 67.677(a/W)^3 + 42.314(a/W)^4 - 8.097(a/W) + 4.495 = \ln \left( \frac{E B V}{P} \right) \]  

Eqn. 3-5

where \( E, B, V, P, \) and \( C_6(a/w) \) are the same parameters as defined in equations 2-5 and 2-7.

The first step of the program was to input the constant of the specimen \( B, V, \) and \( E \) at the testing condition, as well as the obtained \( P \) value. An initial crack length of 1.96 cm (0.77 in) was assumed by the computer, and the correct crack length was obtained by trial-and-error. The computer program, written in Micro-soft BASIC, is listed in detail in appendix A. Finally, combining both the data of the crack growth rate as a function of time and the \( K_I \) as a function of time, the complete \( \frac{da}{dt} = f(K_I) \) curve can be plotted and is shown in Figure 3-34.

However, in most cases, the loading device is not rigid, and the COD is increased as the load decreases during the test. The actual COD during the test is needed in order to calculate the correct crack length. For the SCC test conducted at room temperature, since the COD can, in this case, be measured by the clip gage during the test, the crack length of the specimen can be calculated by the computer program without any problem. However, for the specimens tested in the high temperature solution environment, the COD cannot be measured directly by the clip gage, and further calculation
Laboratory Recorded Data

Converting Load Signal to Load from Loading Device Calibration Curve

Load Device Signal, mV

Time, hours

Normalized by Exact Excitation Voltage

Load, KN

Load Device Signal, mV

Time, hours

(Continued on Next Page)
Figure 3-34 Schematic of the procedures in converting load-signal as a function of time to the crack growth rate as a function of $K_I$ value.
is needed to obtain the true COD value of the specimen during the test. According to the assumption of Novak and Rolfe [17] if the load stud of the loading device is under elastic deflection conditions, $e = \frac{PL}{AE}$, the true COD value, $V_{\text{actual}}$, can be calculated as follows

$$V_{\text{actual}} = \left\{ \left[ \frac{V_o}{a(a+c)} \right] + \left[ \frac{(P_o - P_i) L_s}{E_s A_s} \right] \right\} \cdot \left[ \frac{(a + c)}{a} \right]$$

Eqn. 3-6

where:

- $c$ = distance between the load line and the line for holding the clip gage (1.52 cm (0.6 in) for 1-T modified WOL), see Figure 3-35
- $a_i$ = instantaneous crack length
- $V_o$ = original COD
- $L_s$ = length of load stud
- $A_s$ = cross-sectional area of load stud
- $E_s$ = modulus of elasticity of load stud
- $P_o$ = original load
- $P_i$ = instantaneous load

It is noted that equations 3-5 and 3-6 are recursive functions of the crack length, $a$. In order to obtain the true crack length of the specimen, it is necessary to use an iterative technique.

However, in the present study, the load decrease of the specimens during the tests was very low. Consequently, the change of the COD was very small. Therefore, the COD was
WHERE

\[ V_y = \left( \frac{a}{a + c_1} \right) V \]

Figure 3-35 Schematic of the measurement line of the clip gage and the relation of the COD at the load line \( V_y \) and at measurement line \( V \).
assumed to be a constant during the test, and the COD cali-
6
bration procedures mentioned above were only used as a refer-
ence method. On the other hand, it is noted that the COD of
the specimens loaded with the instrumented loading devices
were decreased significantly at the testing temperature (250
°C) due to the load relaxation of loading devices (detail of
this will be discussed in Section 4.4.2). The COD value used
to calculate the crack length at the testing condition was
calculated by the following equation, which is modified from
equation 2-5.

\[ V = C_6 \frac{P}{EB} \]  

Eqn. 3-7

where \( P \) was the initial load of the specimen at the testing
temperature, \( a \) was the initial crack length of the specimen,
and \( E \) was the Young's modulus of the specimen at the
operating temperature \( (1.76 \times 10^5 \) MPa at 250 °C).

Finally, a computer program, which was developed by
using the linear least-square curve-fitting technique
(Appendix B) [212, 213], is used to find the best straight
line of the crack length/time data in each time period (about
50 hours). The obtained slop of the line is the crack growth
rate of specimen at that time period.
4.1 The DOS, Polarization Behavior, and Corrosion Potential of Sensitized Type 304 Stainless Steel

Figure 4-1 shows the results of the degree of sensitization (DOS) test as a function of the heating time at 50 °C for Heat A Type 304 stainless steel. The DOS vs. heating time curve of this test indicated that the heat treatments chosen for the SCC study were adequate because more prolonged heat treatments did not significantly affect the DOS of the material. The results of DOS tests of previous work [83], using the same test method for the other heat of Type 304 stainless steel, are also superimposed on the Figure 4-1. It seems that the Heat A material used in this study has about the same DOS response as the heat of material tested previously.

Figure 4-2 shows the anodic polarization curve for sensitized Type 304 stainless steel in the deaerated 0.01 m Na_2SO_4 solution at 250 °C. It should be emphasized that this curve was obtained using a blank specimen mounted in the autoclave with the same spatial arrangement as those indicated in Figures 3-6 and 3-28. The curve is similar to that reported elsewhere [16, 133] for small cylindrical specimens, indicating that good potentiostatic control was
Figure 4-1  Current density at 0.29 V$_{SHE}$ on anodic polarization curves for Heat A Type 304 stainless steel in 1 N HClO$_4$ + 0.2 N NaCl as a function of the heating time at 650 °C.
Figure 4-2  Polarization curve for sensitized Type 304 stainless steel in deaerated 0.01 m sodium sulfate solution at 250 °C.
attained with the experimental set-up employed in this work. The corrosion potential of the sensitized Type 304 stainless steel was found to be approximately \(-0.7 \, V_{SHE}\), and was reproducible for all the SCC tests described below. A weak active-passive transition can be noted in Figure 4-2, followed by a small anodic peak, but a passive current of about \(10^{-2} \, mA/cm^2\) is the dominant feature in the potential range that extends from \(-0.5 \, V_{SHE}\) to approximately \(0 \, V_{SHE}\). Above this potential, a transpassive peak, due to the dissolution of chromium, is observed at \(0.1 \, V_{SHE}\), preceding the evolution of \(O_2\) which occurs at higher potentials. The arrows denote potentials at which the SCC tests were conducted.

In addition, the corrosion potential of specimen No. S-6 (650 °C/10 hr) was continuously monitored in a deaerated and aerated testing solution during a test run. The steady state corrosion potentials were about \(-0.7 \, V_{SHE}\) in the deaerated solution and \(0.06 \, V_{SHE}\) in the aerated solution (Figure 4-3). On the other hand, the concentrations of the dissolved oxygen were measured by using a colorimetric method at room temperature at the inlet and the outlet of the autoclave. The obtained values were about 10 ppb dissolved oxygen for the deaerated solution and about 9 ppm dissolved oxygen for the aerated solution. The measured corrosion potentials as a function of the dissolved oxygen concentration are also in good agreement with data obtained
Figure 4-3 The open-circuit potential for specimen No. 304 S-6 tested in aerated 0.01 m sodium sulfate solution at 250 °C.
4.2 SCC Testing in High Temperature Aqueous Environment

The testing conditions for all the high temperature experiments conducted during the course of this study are summarized in Table 4-1. Overall, six test runs were conducted.

4.2.1 Cracks Viewed from Side Surface

Figures 4-4 and 4-5 show the morphology of typical intergranular cracks of the specimens after the SCC tests, as revealed by optical microscopy. These optical micrographs were taken after shaving the side surface to the full depth of the side notch, followed by grinding, and mechanical polishing. Microbranching was a common feature observed during the propagation of intergranular cracks (Figure 4-4). Macrobranchings, seen in Figure 4-5, were also observed for initial $K_I$ values greater than 35 MPa m$^{1/2}$. The occurrence of a single, straight crack is an important requirement in order to apply fracture mechanics techniques to stress corrosion cracking testing. It is difficult to define a meaningful stress intensity value at the crack tip in the presence of macrobranching. Speidel [202] has noted in his SCC study of Type 304 stainless steel in hot MgCl$_2$ solutions that macroscopic crack branching can be avoided by applying a low initial stress intensity, about 1.4 times the minimum stress intensity for Stage II crack growth. In addition, he claimed that when the microbranching is smaller than the
### Table 4-1

Summary of Testing Condition and Crack Growth Rate Results for SCC in 0.01 N Sodium Sulfate Solution at 250°C

<table>
<thead>
<tr>
<th>No. of the Test</th>
<th>Specimen No.</th>
<th>Net Thickness (mm)</th>
<th>Sensitization (hr)</th>
<th>Loading Device</th>
<th>Potential (V SHE)</th>
<th>$K_I$ Range at Test Cond. (MPa$^{rac{1}{2}}$)</th>
<th>Testing Time (hr)</th>
<th>Average Crack Growth Rate (μm/sec)</th>
<th>Maximum Crack Growth Rate (μm/sec)</th>
<th>Remarks</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>S-1</td>
<td>.90</td>
<td>10</td>
<td>LC</td>
<td>-.1</td>
<td>19.3 19.0 280</td>
<td>1x10^{-10}</td>
<td>5x10^{-10}</td>
<td>1.8x10^{-10}</td>
<td>7.9x10^{-10}</td>
</tr>
<tr>
<td></td>
<td>S-2</td>
<td>.90</td>
<td>10</td>
<td>LC</td>
<td>-.1</td>
<td>24.8 24.2 280</td>
<td>1x10^{-10}</td>
<td>5x10^{-10}</td>
<td>1.8x10^{-10}</td>
<td>7.9x10^{-10}</td>
</tr>
<tr>
<td>2</td>
<td>S-3</td>
<td>.90</td>
<td>10</td>
<td>LC</td>
<td>-.1</td>
<td>26.9 26.5 500</td>
<td>2.8x10^{-10}</td>
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<td>0</td>
<td>27.5 27.2 500</td>
<td>1.3x10^{-10}</td>
<td>1.3x10^{-10}</td>
<td>3.3x10^{-10}</td>
<td>3.3x10^{-10}</td>
</tr>
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<td></td>
<td>S-6</td>
<td>.90</td>
<td>10</td>
<td>Bolt</td>
<td>-0.69</td>
<td>26.4 26.4 500</td>
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<td>&lt;0</td>
<td>&lt;0</td>
<td>&lt;0</td>
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<td>Bolt</td>
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<td>23.6 23.1 530</td>
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<td>Bolt</td>
<td>-0.2</td>
<td>23.2 23.2 530</td>
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<td>1.1x10^{-10}</td>
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<tr>
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<td>24</td>
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<td>29.3 28.1 650</td>
<td>9.4x10^{-10}</td>
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<td>10</td>
<td>Bolt</td>
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<td>35.6 35.5 650</td>
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<td>Bolt</td>
<td>0.3</td>
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<td>6.8x10^{-10}</td>
<td>6.8x10^{-10}</td>
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<td>S-24</td>
<td>.90</td>
<td>24</td>
<td>Bolt</td>
<td>-0.3</td>
<td>27.9 27.9 560</td>
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<td>&lt;0</td>
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<td>Bolt</td>
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<td>27.3 26.9 560</td>
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<td>21.3 19.7 560</td>
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<td>24</td>
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<td>S-31</td>
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<td>24</td>
<td>IIIB</td>
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<td>22.6 22.1 234</td>
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<td>7.1x10^{-10}</td>
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<td></td>
</tr>
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<td>S-32</td>
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<td>IIIB</td>
<td>0</td>
<td>20.3 20.2 312</td>
<td>1.3x10^{-10}</td>
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<td>Potentiostat turned off after 312 hrs. testing.</td>
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</tr>
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<td>S-33</td>
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<td>24</td>
<td>IIIB</td>
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<td>21.1 20.8 670</td>
<td>2.0x10^{-10}</td>
<td>2.0x10^{-10}</td>
<td>Potentiostat turned off after 312 hrs. testing.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>W-1</td>
<td>.90</td>
<td>*</td>
<td>Bolt</td>
<td>0</td>
<td>21.7 21.3 670</td>
<td>2.0x10^{-10}</td>
<td>2.0x10^{-10}</td>
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<td>W-2</td>
<td>.865</td>
<td>*</td>
<td>Bolt</td>
<td>0</td>
<td>24.6 24.6 670</td>
<td>1.3x10^{-10}</td>
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<td>1.3x10^{-10}</td>
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</tr>
<tr>
<td></td>
<td>W-3</td>
<td>.865</td>
<td>*</td>
<td>Bolt</td>
<td>0</td>
<td>26.4 22.7 670</td>
<td>1.5x10^{-9}</td>
<td>1.5x10^{-9}</td>
<td>1.5x10^{-9}</td>
<td>1.5x10^{-9}</td>
</tr>
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</table>

*See Table 3-3
Figure 4-4 Side surface of specimen tested in deaerated 0.01 m sodium sulfate solution at 250 °C under a potential of 0 V SHE, at an initial $K_I$ value of 27.5 MPa m$^{1/2}$, showing small branching.
Figure 4-5 Side surface of specimen tested in deaerated 0.01 m sodium sulfate solution at 250 °C under a potential of 0.2 V \text{SHE}, at an initial \( K_I \) value of 42.2 MPa m^{1/2}, showing pronounced macrobranching.
size of the plastic zone at the tip of the main crack, the fracture mechanics approach is a valid one.

The microstructure at the crack tip on the side surface of specimen No. S-1 after the test was revealed by etching, as shown in Figure 4-6. The etching solution was composed of 10 ml nitric acid, 10 ml acetic acid, 15 ml HCl and 2 to 5 drops glycerol. The etched microstructure indicated that no IGSCC occurred on the side surface, and a plastic deformation zone whose size was about 50 to 80 microns was revealed at the fatigue pre-crack tip. Because the size of the plastic deformation zone is proportional to the square of the stress intensity value at the crack tip [203], the plastic deformation zone size for the specimen loaded between 20 and 35 MPa \( m^{1/2} \) should be between 100 and 250 micron. This plastic zone size is larger than the micro-branchs observed in this study.

In addition, as revealed in Figure 4-7, intergranular side-branchings often occurred at the fatigue pre-crack, particularly at high anodic potentials (0.2 to 0.3 \( V_{\text{SHE}} \)). This phenomenon indicates that, at that applied potential range, an intergranular attack could take place in a region with a very low stress intensity factor on the side surface of the specimen.
Figure 4-6 Side surface of specimen tested in deaerated 0.01 m sodium sulfate solution at 250 °C under a potential of -0.1 V_{SHE}, at an initial $K_I$ value of 19 MPa m$^{1/2}$, showing the etched microstructure. (Composition of etching solution is: 10 ml nitric acid, 10 ml acetic acid, 15 ml HCl and 2 to 5 drops glycerol.)
$S-15$

$E = 0.2 \ V_{SHE}$

$K_I = 42.2 \ MPa \ m^{1/2}$

Figure 4-7  Side surface of specimen tested in deaerated 0.01 m sodium sulfate solution at 250 °C under a potential of $0.2 \ V_{SHE}$, at an initial $K_I$ value of 42.2 MPa m$^{1/2}$, showing pronounced side-branching.
4.2.2 Cracks Viewed from Fracture Surface

Low magnification views of the fracture surface of some specimens after testing, followed by a final fatigue fracture in air, are shown in Figure 4-8. In these fractographs, the pre-test fatigue fracture surface and the stress corrosion cracked surface are both revealed as a dark area. A curved fatigue crack front is observed, which is typical of many ductile materials, such as austenitic stainless steel (see, as an example, Figure 7 and 8 in Ref. 16). It is also of interest to note that the shape of the intergranular crack front did not follow that of the fatigue pre-crack, but instead was found to be extremely dependent upon potential. This is schematically illustrated in Figure 4-9. Details of this will be discussed in Section 5.2.

Figure 4-10 shows a high magnification SEM micrograph of the fractured specimen. The propagation region of the intergranular crack is bound by the fatigue fracture surfaces developed by cyclic loading in air before and after testing. A further examination of the SEM fractograph reveals two important points. Firstly, except for a few cases in which the intergranular attack at one side of the specimen is more severe than at the other side the IGSCC of most of the specimens (Figure 4-11) is symmetrical to the center of the fractured surface. This indicates that, although the reference electrode is at one side of the specimen (see Figure 3-28), the corrosion potential at both
Figure 4-8 Low magnification fractographs revealing the effect of potential on the shape of the intergranular crack front for specimens tested in 0.01 m sodium sulfate solution at 250 °C.
Crack Growth Direction

(a) $-0.3 \text{ V}_{\text{SHE}}$
(b) $-0.2 \text{ to } \sim 0 \text{ V}_{\text{SHE}}$
(c) $0.2 \text{ V}_{\text{SHE}}$
(d) $0.3 \text{ V}_{\text{SHE}}$

Figure 4-9 Schematic drawing showing the effect of applied potential on the shape of the intergranular crack front for specimens tested in 0.01 m sodium sulfate solution at 250 °C.
Figure 4-10 SEM fractograph showing the typical appearance of the intergranularly cracked area for specimens tested in 0.01 m sodium sulfate solution at 250 °C.
Figure 4-11 SEM fractograph showing the symmetrical crack front for specimens tested in 0.01 m sodium sulfate solution at 250°C. a) Left edge, b) center, and c) right edge.
side surfaces of the specimen is about the same with respect to the reference electrode. In addition, the maximum length of the intergranular crack seems to be dependent upon the applied potential, as will be discussed in more detail below, but it should be emphasized that no detectable crack growth was observed at potentials lower than \(-0.2\) \(V_{\text{SHE}}\).

### 4.2.3 Crack Growth Rate

The average length of the intergranular crack, as calculated by using equation 3-1, was divided by the exposure time under the applied potential to determine an average crack growth rate. A plot of this average crack velocity as a function of \(K_I\) is shown in Figure 4-12 for various applied potentials within the potential range in which crack growth was observed. It can be seen that most of the data points lie within two curves, adopted as lower and upper boundaries, which reveal two regions of \(K_I\) dependence. At low \(K_I\) values, crack velocity seems to be extremely dependent upon \(K_I\), whereas at \(K_I\) values greater than 20-25 MPa m\(^{1/2}\), it becomes almost independent of \(K_I\). However, the precise effect of potential on crack velocity cannot be discerned from this plot. This is due to the specific influence of the potential on the shape of the intergranular crack front. However, when the maximum crack velocities, calculated by dividing the maximum crack length by the testing times, are plotted as a function of \(K_I\), as in Figure 4-13, the effect of potential and also to a lesser extent of
Figure 4-12 Average crack growth rate as a function of $K_I$ at various potentials for sensitized Type 304 stainless steel in 0.01 m sodium sulfate solution at 250 °C.
Figure 4-13 Maximum crack growth rate as a function of $K_I$ at various potentials for sensitized Type 304 stainless steel in 0.01 m sodium sulfate solution at 250 °C.
heat-treatment time becomes apparent. From Figures 4-12 and 4-13, it appears that a minimum value of $K_I$ exists below which the crack growth rate becomes smaller than $10^{-11} \text{ m/s}$. This value, $K_{ISCc}$, seems to decrease with increasing applied potential. The data for the average and the maximum crack growth rates are listed in Table 4-1.

The effect of potential on crack velocity can be more easily seen in Figures 4-14 and 4-15, where the average crack velocity and maximum crack velocity are plotted as a function of potential for specimens loaded to different $K_I$ values. From both figures, it is apparent that a critical potential exists, between -0.2 and -0.3 $V_{SHE}$, below which intergranular crack growth does not occur or is extremely slow. The crack growth rate increases with increasing potential, attaining a maximum around $0 V_{SHE}$. Since the crack growth rates are in most of the cases lower than $1 \times 10^{-9} \text{ m/s}$, the total crack lengths are less than 2 mm during the entire testing time. Therefore, contrary to initial assumptions, the decreases in load were small. As a consequence, the decreases in $K_I$ were, at the most, about 2% for almost all the specimens, as seen in Table 4-1.

As will be discussed in detail in the Section 4.4.4, the performance of the instrumented loading devices was impaired by various unexpected problems. Nevertheless, some successful tests were conducted. To illustrate the results obtained with the instrumented loading devices, Figure 4-16
Figure 4-14 Effect of potential on the average crack growth rate for sensitized Type 304 stainless steel loaded at various initial $K_I$ values in 0.01 m sodium sulfate solution at 250 °C.
Figure 4-15 Effect of potential on the maximum crack growth rate for sensitized Type 304 stainless steel loaded at various initial $K_I$ values in 0.01 m sodium sulfate solution at 250 °C.
Figure 4-16 Relaxation of load (measured as load-signal of the IIB) as a function of time during intergranular crack propagation for the WOL specimen at an applied potential of $0 \text{V}_{\text{SHE}}$.  

Load Relaxation of SP No. 31  
In 0.01N Na$_2$SO$_4$  
$250^\circ \text{C}$  
$0 \text{V}_{\text{SHE}}$

Correlation Coefficient is 0.989
shows a typical variation of load signal as a function of time as measured by the internal instrumented bolt (IIB). After an initial loading to a value of $K_I = 22.9 \text{ MPa m}^{1/2}$, a potential of $0 \text{ V}_{\text{SHE}}$ was applied to specimen No. S-31. Despite some fluctuations, the load decreased almost linearly with time as the crack grew. No detectable induction time was observed. In addition, following the procedures outlined in Figure 3-33 and the descriptions listed in Section 3.4, crack length, crack growth rate and $K_I$ were calculated at three different times, as shown in Figure 4-17. Data points from specimen No. S-33 loaded initially to a lower $K_I$ value are also shown in Figure 4-17. For the purpose of comparison, average crack growth rates, as calculated from the IIB data and from measurements of crack length on fracture surfaces, are represented as horizontal bars in Figure 4-17. These results indicate that the load relaxation method allows the crack growth rates to be determined with relatively good accuracy.

4.2.4 Current and pH Variation

Figure 4-18 shows a typical set of curves for current density variation during the 4th test. The average current density was obtained by dividing the total current with the total surface area of the specimen and the attached loading devices. There are two important features which appear on this set of curves. Firstly, there is a significant difference in current density for specimen No. S-11 and No. S-
Figure 4-17 Crack growth rate calculated from the load relaxation data using the IIB as a function of $K_I$ for two modified WOL specimens tested at two initial $K_I$ values at $0 \text{ V}_{\text{SHE}}$. 

Sensitized Type 304 Stainless Steel
0.01 m Na$_2$SO$_4$
$T=250^\circ$C
$E=0 \text{ mV}_{\text{SHE}}$
Figure 4-18 Variation of current density for specimens tested in deaerated 0.01 m sodium sulfate solution at 250 °C.
13 (Figure 4-18(a)) as well as for specimen No. S-15 and No. S-16 (Figure 4-18(b)). It can be seen that the only difference in the testing condition between the specimens with high and low current levels is the sensitization time of the specimens. Another feature is that there is a dramatic change in the current density for specimen S-17 (Figure 4-18(c)). Table 4-2 further summarizes the average current density and total charges, as well as the average crack growth rate of the specimens conducted in this study.

The data in Table 4-2 and Figures 4-18(a) and 4-18(b) reveal that the average crack growth rate has a close relationship with the average current density. Generally speaking, the current density increases as the crack growth rate increases, as shown in Figure 4-19. Also, a crack growth rate faster than $1 \times 10^{-10}$ m/s would generate a current density higher than $10^{-3}$ mA/cm$^2$. All these observations further indicate that the crack tip contributes the major portion of the current measured during the test when a fast IGSCC occurs at the tip. Since the actual size of the film rupture area at the crack tip is very difficult to determine, an actual current density generated at the crack tip can not be calculated. However, it is to suppose reasonable guess that the current density generated at the crack tip should be at least two orders of magnitude higher than the average current density.
Table 4-2 Summary of Testing Current Results

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Sensitization (hr.)</th>
<th>Potential ($V_{SHE}$)</th>
<th>Average Current Density ($\mu A/cm^2$)</th>
<th>Total Charge (kc)</th>
<th>Average Crack Growth Rate ($10^{-10}$ m/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-3</td>
<td>10</td>
<td>-0.1</td>
<td>6.4</td>
<td>10.4</td>
<td>2.8</td>
</tr>
<tr>
<td>S-4</td>
<td>10</td>
<td>0</td>
<td>11</td>
<td>17.6</td>
<td>1.2</td>
</tr>
<tr>
<td>S-11</td>
<td>10</td>
<td>0.2</td>
<td>1.7</td>
<td>3.1</td>
<td>1.0</td>
</tr>
<tr>
<td>S-13</td>
<td>24</td>
<td>0.2</td>
<td>27</td>
<td>68</td>
<td>6</td>
</tr>
<tr>
<td>S-15</td>
<td>24</td>
<td>0.2</td>
<td>16</td>
<td>38</td>
<td>9</td>
</tr>
<tr>
<td>S-16</td>
<td>10</td>
<td>0.2</td>
<td>0.03</td>
<td>0.08</td>
<td>0.54</td>
</tr>
<tr>
<td>S-17</td>
<td>10</td>
<td>0.3</td>
<td>13</td>
<td>32.6</td>
<td>2.5</td>
</tr>
<tr>
<td>S-24</td>
<td>24</td>
<td>-0.3</td>
<td>0.84</td>
<td>1.69</td>
<td>0</td>
</tr>
<tr>
<td>S-25</td>
<td>24</td>
<td>-0.2</td>
<td>12</td>
<td>23.7</td>
<td>2</td>
</tr>
<tr>
<td>S-31</td>
<td>24</td>
<td>0</td>
<td>15</td>
<td>12.6</td>
<td>4</td>
</tr>
<tr>
<td>S-32</td>
<td>24</td>
<td>0</td>
<td>4</td>
<td>4.7</td>
<td>1.3</td>
</tr>
<tr>
<td>S-33</td>
<td>24</td>
<td>0</td>
<td>7</td>
<td>12</td>
<td>2.0</td>
</tr>
</tbody>
</table>
Figure 4-19 The average current density as a function of the average crack growth rate for specimens tested in deaerated 0.01 m sodium sulfate solution at 250 °C
Following the same argument, the current drop of specimen S-17 after 185 hours of testing may be explained by the fact that the crack of this specimen was arrested at that time. A possible reason for the crack arrest may be explained in the following manner. As shown in Figure 4-8, the crack front on specimen No. S-17 had a special shape caused by the fact that the center of the specimen had a higher crack velocity than that at the edges. Due to this crack advancement, the load, instead of being equally distributed along the crack front, became intensified at the edges of the crack front. Consequently, the $K_I$ value dropped dramatically at the center of the specimen, and this drop also induced the crack arrest and current density decline.

The pH values of the inlet and outlet solutions were also monitored by the data acquisition system for each test run. At the inlet, the pH value of the testing solution, a 0.01 m sodium sulfate solution, varied with the dissolved oxygen concentration. Its value changes from 5.7 in an aerated condition to 8.0 in a fully deaerated condition. On the other hand, the pH value at the outlet, except for a few dramatic variations (Figure 4-20 (a)), was kept in between 8.5 and 9.5. In a further analysis of the testing data, it was found that the pH variation of the outlet solution was related to the applied current of the testing specimen. For example, the current density peaks of specimen No. S-15
Figure 4-20 (a) Variation of pH for the inlet and outlet solution during the 4th SCC test in deaerated 0.01 m sodium sulfate solution at 250 °C. (b) Variation of current density for specimen S-15 in the same environment.
(Figure 4-20 (b)) always occurred about one or two hours before the increase in the pH value of the outlet solution. This phenomenon suggests that the solution was acidified when a fast electrochemical reaction occurred at the crack tip of the specimen.

4.3 Specimen Machined from Welded Plate

4.3.1 Weld Structure and The DOS

Figure 4-21 shows photographies of the etched structures of the cross-section of the welded plate before and after post-weld heat treatment (550 °C/24 hr). Although the weld structure was designed to have a straight fusion line, as well as a straight HAZ, the uneven heat input between each welding pass during the welding process made the fusion line as well as HAZ slightly rippled.

Two methods were used to examine the regions which were susceptible to the IGSCC. The cross-sections of the as-welded and the as-welded + post-weld heat treatment specimens were first examined by the oxalic acid etch test. Figure 4-22 shows the optical micrographs of the etched structure of the specimens at three different regions, namely, the weld fusion line, HAZ, and base metal. The ditch structure, which appears in the HAZ and the region near the fusion line of the as-welded + post-weld heat treated specimen, indicates that these regions are prone to intergranular attack. On the other hand, the end grain pit and the step structures which appear at the other regions
Figure 4-21 The etched welded structures of the welded plate, a) was etched by a solution of 10 ml nitric acid, 10 acetic acid, 15 ml HCl and 2 to 5 drops glycerol; and b) was etched by the oxalic acid test.
Figure 4-22 Optical micrograph of as-welded and as-welded + 550°C/24 hr specimens after the oxalic acid test.
of the specimens ensure that these areas are immune to intergranular attack. The DOS, measured by the sequential polishing and measurement technique in Figure 4-23, confirms the observations mentioned above. The current density of the anodic polarization test in a perchloric acid solution with 0.2 N NaCl indicates that, for the as-welded + post-weld heat treated specimen, the regions between the weld fusion line and the line about 0.5 cm away from the weld center line are all susceptible to IGSCC. On the other hand, for the as-welded specimen, only the region which is inside the region, which is about 0.45 to 0.55 cm away from the weld center line, may susceptible to IGSCC. However, In addition, the maximum current density of the as-welded + post-weld heat treated specimen, 1.5 mA/cm², is higher than that of the as-welded specimen, i.e. 1.1 mA/cm². In comparing these current density data to the Figure 4-1, it can be seen that the DOS of the these specimens cerrosponds to those specimens sensitized at 650 °C for 3 to 10 hours.

Finally, the current density of the base metal of the specimen, which was post-weld heat treated, is also slightly higher than that of the base metal of the as-welded specimen. However, the DOS represented by that current density value, 0.1 mA/cm² is well below the critical value to induce IGSCC. This result implies that the post-weld heat treatment is not severe enough to sensitize the un-welded structure.
Figure 4-23 Current density at $0.29 \ V_{\text{SHE}}$ on anodic polarization curves for as-welded and as-welded + 550 °C/24 hr specimens in 1 N $\text{HClO}_4 + 0.2$ N NaCl as a function of the distance away from the weld center line.
4.3.2 SCC Test in High Temperature Aqueous Environment

The SCC testing conditions of the specimens, No. W-1 (as-received + 650 °C/24 hr), W-2 (as-welded), and W-3 (as-welded + 550 °C/24 hr) machanied from the welded plate (Heat B material) are listed in Table 4-1.

Figure 4-24 shows the cracks on the side surface of the W-2 and the W-3 specimens. No IGSCC is observed at the tip of the fatigue pre-crack of the W-2 specimen. However, an extraordinarily severe degree of intergranular attack appeared on the side surface of the W-3 specimen. For that specimen, not only did the extended intergranular crack have a large amount of macrobranchings, but many intergranular side branchings also occurred at the fatigue pre-crack.

The low magnification photographs of the fracture surface of the W-1, W-2, and W-3 specimens are shown in Figure 4-25. The shape of the curved fatigue crack front of the W-2 and W-3 specimens is quite different from the shape of the W-1 specimen and the regular specimens mentioned before (see Figure 4-8). It seems that the welding residual stress may play an important role in altering the shape of the fatigue crack front. Generally speaking, for a double-bevel-groove butt joint, a high tensile-type residual stress is believed to be distributed at the region near both side surfaces of the weld structure [209]; on the other hand, a compression-type residual stress is located at the center of the weld junction.
Figure 4-24 Side surface of W-2 and W-3 specimens after testing in 0.01 m sodium sulfate solution at 250 °C for 670 hours.
Figure 4-25 Low magnification fractographs of specimens machined from the welded plate after testing in 0.01 m sodium sulfate solution at 250° C for 670 hours.
The crack growth rates of Specimen No. W-2 and W-3 are also different from the other specimens. The W-2 specimen did not show any detectable crack growth during the total testing time (670 hours) whereas the W-3 specimen had a maximum crack growth rate of $3.8 \times 10^{-9}$ m/s. This was the highest crack growth rate measured during the course of this study. On the other hand, the W-1 specimen showed a maximum crack growth rate of $5.4 \times 10^{-9}$ m/s, which is similar to that obtained under equivalent conditions for Heat A specimens. The test results of Heat B specimens are also tabulated in Table 4-1.

Figure 4-26 shows the transmission electron micrographs of the carbides at the grain boundaries of the specimens after the SCC test. It is clearly shown that the carbides of the specimen sampled from the HAZ of the W-3 specimen are smaller and more widely spaced than those of the specimen sampled from the W-1 specimen (650 °C/24 hr). This observation agrees with the result obtained by Ruther et al. [101]. They found that the specimen sensitized at 700 °C for 12 hours (medium sensitized) has larger carbides than the specimen sensitized at 700 °C/0.25 hr + 500 °C/24 hr (lightly sensitized, simulate as-welded + LTS heat treatment). Due to some difficulties in technique, the concentration profiles across the grain boundary of these two specimens could not be determined in this study. However, according to the STEM results of Ruther et al., the medium
Figure 4-26 TEM of the carbides at the grain boundaries of Type 304 stainless steel (a) sampled from W-1 specimen (b) sampled from the HAZ of W-3 specimen.
sensitized specimen at 700 °C for 12 hrs has a much wider depleted zone than the lightly sensitized one (about 80 vs 18 nm). But, due to the limitation of the electron microscope (the minimum electron beam size about 12 to 16 nm) they could not find the difference of the depth of the Cr-depleted zone between those two specimens. Therefore, the observations of the STEM work mentioned above indicate that it is difficult to explain why the W-2 specimen has the fastest crack growth rate of all the tested specimens. A detailed discussion of this will be given in Section 5.3.

4.4 Development and Testing of Instrumented Loading Devices

4.4.1 Linearity and Sensitivity

Figure 4-27 shows the typical room temperature calibration curves for the loading devices employed in this study. The calibration of the load cell (LC) shows that this type of device exhibits a very good linearity in the output signal over the load range of interest. On the other hand, the addition of steel balls (6.35 mm dia. Type 410 stainless steel) either at both ends (Figure 3-18) or at one end of the load stud (Figure 3-21) were necessary to attain linearity in the output signal for the external instrumented bolt (EIB) and the internal instrumented bolt (IIB).

The calibration curves shown in Figure 4-27 also reveal that the load cell has the highest sensitivity for load monitoring. With a 10-volt excitation voltage, the load cell
Figure 4-27 Typical calibration curves for the instrumented loading devices used in this study.
signal varies by about 35 mV when the load changes from 0 to 26.7 kN (6000 lbf), corresponding to a sensitivity of about 0.76 kN/mV. Since the data acquisition system used in this study can measure a voltage signal in the microvolt range, the limit of detection for the load cell is sufficiently low to measure a load variation of about 1N (0.22 lbf). The limit of detection for the EIB and the IIB was about 2.7 N (0.6 lbf) and 1.3 N (0.37 lbf), respectively.

Table 4-3 shows typical results for shunt calibration of an IIB at room temperature and at 250 °C. The shunt resistance listed in the table is calculated by the following equation:

\[ R = G.F. \times \varepsilon \times R_g \]  \hspace{1cm} \text{Eqn. 4-1}

\[ R_s = R_g \left( R_g - \Delta R \right) / \Delta R \]  \hspace{1cm} \text{Eqn. 4-2}

where \( \varepsilon \) = A known compressive strain

\( \Delta R \) = Expected resistance variation

\( R_g \) = Resistance of strain gage being shunted (122.3 Ω)

\( G.F. \) = Gage factor of the strain gage (5.0 at 25 °C, 4.6 at 250 °C)

\( R_s \) = Value of shunt resistor

These calculated shunt values which, when installed across the strain gage of the IIB, simulate a reduction in the resistance of the strain gage equivalent to the compressive strain are listed in the first column of the table. The obtained load-signal of the shunt calibration is plotted in
Table 4-3

Values of Shunt Resistance and the Obtained Load-Signal for IIB

<table>
<thead>
<tr>
<th>Equivalent Compressive Strain (µ Strain)</th>
<th>Room Temperature</th>
<th>250°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Shunt Resistance</td>
<td>Load-Signal</td>
</tr>
<tr>
<td></td>
<td>(Ω)</td>
<td>(mV)</td>
</tr>
<tr>
<td>300</td>
<td>89409.2</td>
<td>2.82</td>
</tr>
<tr>
<td>500</td>
<td>53596.6</td>
<td>4.78</td>
</tr>
<tr>
<td>700</td>
<td>38248.3</td>
<td>6.75</td>
</tr>
<tr>
<td>900</td>
<td>29721.5</td>
<td>8.72</td>
</tr>
<tr>
<td>1000</td>
<td>26737.1</td>
<td>9.70</td>
</tr>
<tr>
<td>1200</td>
<td>22260.6</td>
<td>11.67</td>
</tr>
<tr>
<td>1400</td>
<td>19063</td>
<td>13.64</td>
</tr>
<tr>
<td>1600</td>
<td>16664.8</td>
<td>15.62</td>
</tr>
<tr>
<td>1800</td>
<td>14799.6</td>
<td>17.59</td>
</tr>
<tr>
<td>2000</td>
<td>13307.4</td>
<td>19.57</td>
</tr>
</tbody>
</table>
Figure 4-28 as a function of the equivalent compressive strain. This plot indicates that the load-signal is varied linearly with the compressive strain at room temperature as well as at 250 °C. In addition, the corresponding sensitivity of the IIB (calculated from the slope of the plot) at the higher temperature, 1.12 kN/mV, is about the same as that at the room temperature, 1.16 kN/mV. Therefore, in order to simplify the calculation the sensitivity of the IIB at the higher temperature is assumed to be the same as that at room temperature. This assumption is also implied by the gage manufacturers. They claimed that the reduction in the sensitivity of the loading devices at the higher temperature is almost compensated for the sensitivity supplement. The reduced sensitivity arises from the decrease in the gage factor whereas the sensitivity supplement is due to the decrease in the young's modulus of the load stud material at that temperature.

4.4.2 Stability

A typical stability test for the IIB as a function of time for both room and high temperature is shown in Figure 4-29. Following an initial decay due to thermal relaxation and the difference between the thermal expansion coefficients of the materials used in the IIB and the specimen, Inconel X-750 and Type 304 stainless steel respectively, the load was very stable at both room temperature and 250 °C. Neither a significant signal drift nor zero shift was
Figure 4-28 Typical shunt calibration curves for the IIB at room temperature and at 250 °C.
Figure 4-29 Typical stability test at room temperature and at 250 °C for the IIB.
observed during the test. However, the stability of the LC and EIB were not as good as that of the IIB. Table 4-4 summarizes the results of the stability tests for these loading devices. The signal drift and zero shift depend on the strain level, the quality of the strain gage bonding, and the gage and carrier material. Since the IIB was constructed with a better strain gage material (Pt-W), and was completely embedded in the load stud by silver brazing, it had a much better stability than the LC and the EIB. On the other hand, the load relaxation at the testing temperature (250 °C) was related to the following two causes. Firstly, young's modulus for the load stud decreased as the testing temperature increased, so that it supported a smaller load at the higher temperature than it did at room temperature. Secondly, the material of the load stud of the instrumented loading devices (17-4 PH stainless steel and Inconel X-750 alloy) has a lower thermal expansion coefficient (about 13.5×10^{-6}/cm/cm/°C at 250 °C) than that of the specimen material (about 18×10^{-6}/cm/cm/°C at 250 °C for Type 304 stainless steel) [204]. This difference also reduced the COD as well as the load of the specimen at the testing temperature.

During the test, the signal stability was affected by two other factors, namely the quality of the dummy resistors (which includes the standard temperature coefficient and the stability of the resistor) and the channel stability of the
Table 4-4

Summary of Stability Tests for Instrumented Loading Devices

<table>
<thead>
<tr>
<th>Loading Devices</th>
<th>Number of Devices Tested</th>
<th>Zero Drift at 250°C</th>
<th>Zero Shift After Load Released</th>
<th>Load Relaxation at 250°C Due to Thermal Effects (% of original load)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LC</td>
<td>10</td>
<td>~0.2 mV/100 hr</td>
<td>~0.5 mV</td>
<td>~25</td>
</tr>
<tr>
<td>EIB</td>
<td>2</td>
<td>~0.5 mV/100 hr</td>
<td>~0.2 mV</td>
<td>~35</td>
</tr>
<tr>
<td>IIB</td>
<td>3</td>
<td>~0</td>
<td>~0</td>
<td>~25</td>
</tr>
</tbody>
</table>
data acquisition system. As mentioned before (Section 3.3.3) in order for the signal of the instrumented bolts to be read directly by the data acquisition system, two dummy resistors were connected to the instrumented bolts to form a full bridge circuit. Therefore, the stability and temperature coefficient of the resistors also affected the stability of the load-signal (see Figure 4-30). Since the resistance of the carbon film-type precision resistor is sensitive to a variation in the temperature (its T.C. is 20 ppm/°C), the recorded EIB signal varied about 2 mV a day due to a variation in the room temperature. The variation in room temperature in this laboratory was about 5 °C. On the other hand, the variation of the signal was less than 0.04 mV when the instrumented bolt was connected to the wire-type resistors (its T.C. is 5 ppm/°C). Finally, in order to get the best stability performance, a pair of hermetically-sealed Vishay-type resistors (distributed by the Micro-Measurement Co. Ser. No. H2-120-01) was selected whose T.C. is 1 ppm/°C and whose resistance variation is less than 5 ppm per year. The effect of these resistors is already shown in Figure 4-29. Apart from the quality of the resistors, the stability of the recorded load-signal was also affected by a high-level signal at the channel immediately before the channel recording this load-signal. For example, when Channel 5 is used to record a load-signal, a high-level signal (higher than 0.5 Volt) recorded at Channel 4 will alter that load-
Figure 4-30 The effect of the different types of dummy resistors and signal insulation on the load-signal stability of the EIB.
signal. To avoid this problem, that channel can be shorted by a jumper lead or used to record a low-level signal (below 100 mV).

4.4.3 Crack Growth Measurement at Room Temperature

In order to study the effectiveness of the load relaxation method for measuring crack length, one modified WOL specimen, sensitized at 650 °C for 24 hours, was loaded with the IIB and tested in an aerated 0.5 M sodium thiosulfate solution at room temperature under an applied potential of 0.15 V_{SHE}. It has been reported [205, 206] that this solution induces fast crack growth rates (about $10^{-6}$ m/s). The relaxation of the load and the intergranular crack length as a function of time are shown in Figure 4-31. The crack growth a length of, 0.6 cm, measured over a period of 100 hours and calculated from the load relaxation method (Section 3.5), agrees very well with the value of 0.62 cm measured optically. It can be concluded that the crack growth length, and therefore the crack growth rates of the modified WOL specimens, could be accurately measured by using the IIB.

4.4.4 High Temperature Aqueous Environment Testing

The loading devices developed for this study experienced several problems in the normal SCC testing environment (0.01 m sodium sulfate at 250 °C). These problems are discussed in the following section.
Figure 4-31 Load relaxation and intergranular crack growth as a function of time for sensitized Type 304 stainless steel in 0.5 M Na$_2$S$_2$O$_3$ solution at room temperature under an applied potential of 0.15 $V_{SHE}$.
4.4.4.1 Load Cell

The major problem with the load cell was the entrance of the solution into the load cell chamber due to stress corrosion cracking at the heat-affected zone of the weld bead, as shown in Figure 4-32. Only one out of ten load cells could endure the total testing period (about 600 hrs). Another problem was the susceptibility of the bolt material, 17-4 PH stainless steel, to stress corrosion cracking. In one test, specimen No. S-27, the threaded area of the load cell's bolt broke during testing. Finally, a lead wire was fractured when one of the specimens was mounted inside the autoclave. The lead wire was made of MgO insulated cable sheathed with a 0.24 cm Type 304 stainless steel tube. Due to strain hardening, it became rigid and brittle after repeated bending in at same position. Due to these problems, the load cell was found to be inadequate for this study.

4.4.4.2 EIB

The signal drift at the operating temperature (about 0.5 mV in 100 hrs) was the major problem of the EIB. This drift was mainly caused by metallurgical changes (phase transformations and annealing) in the strain-gage alloy [207]. Usually, the drift rates depend on both the testing temperature (see Figure 3-23) and the strain level. The observed drift rate mentioned above corresponded to a crack growth rate of about $2.5 \times 10^{-8}$ m/s. Because, the crack
Figure 4-32 Photograph of a failed load cell. (The arrows indicate the locations susceptible to failure.)
growth rates measured in this study were between $10^{-11}$ and $10^{-9}$ m/s, the error which was introduced by the signal drift was too large. In addition, $K_I$ dropped significantly due to the load relaxation at the operating temperature. As shown in Table 4-4, the load at the operating temperature was only about 35% of the original load at room temperature. For example, an initial $K_I$ value of 25 MPa m$^{1/2}$ at room temperature would be reduced to a $K_I$ value lower than 17 MPa m$^{1/2}$ at 250 °C. Hence, the initially applied $K_I$ value may not be high enough to induce stress corrosion cracking. This may be the reason for the very low crack growth rate observed for specimen S-30 (Table 4-1). Finally, several shallow pits were observed on the lead wires (Type 347 stainless steel) of the EIB, after 600 hours in the operating environment. This observation suggests that Type 347 stainless steel is not a reliable material for lead wire.

4.4.4.3 IIB

The major problem was the propensity towards IGSCC of the lead wire material (annealed Inconel 600) in a stressed area produced by bending (see Figure 4-33). This could be prevented by coating the head of the bolt and lead wire with PTFE material. Except for this problem, IIB performed extremely well under the high temperature aqueous testing environment. It is worth mentioning that, due to its stability and high sensitivity, the IIB can measure the crack growth rate of a modified WOL specimen to as low as $10^{-12}$
Figure 4-33 Photograph of a failed IIB.
4.4.5 Field Testing

Five field tests have been completed while a sixth is still in progress. Each field test lasted about two months. The instrumented loading devices were loaded to about 22.3 to 24.5 kN (5000 to 5500 lbf) for each field test. No significant load-signal relaxation or significant crack growth was observed in those completed tests. As mentioned previously, the load-signal was recorded by the computer system of the power station. The data were recorded for 5 seconds, and were averaged hourly as well as daily by the computer. Figure 4-34 shows typical data recorded hourly and daily. Table 4-5 further lists the daily standard deviation of the load-signal calculated for each loading device and the number of test-runs that have been conducted. As indicated in the figure, the daily signal drift of the EIB and load cell at the testing temperature (150 °C) was less than those observed at 250 °C (see Table 4-4). However, according to the data recorded hourly, the signal stability of these two types of devices was not as good as that of the IIB. In addition, after about four field tests, two load cells had broken down. Obviously, the durability of the load cells is not as good as that of the EIB which functioned properly after the same number of the test runs.
Figure 4-34 Typical load-signal variation of the instrumented loading devices during the field test.
Table 4-5

Summary of The Signal Stability of Instrumented Loading Devices in The Field Test

<table>
<thead>
<tr>
<th>Type of Loading Devices</th>
<th>Number of Test Run</th>
<th>Max. Daily Standard Deviation (mV)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load Cell No. 1</td>
<td>4</td>
<td>0.20</td>
<td>failed</td>
</tr>
<tr>
<td>Load Cell No. 2</td>
<td>4</td>
<td>0.08</td>
<td>failed</td>
</tr>
<tr>
<td>EIB No. 1</td>
<td>4</td>
<td>0.28</td>
<td>O.K.</td>
</tr>
<tr>
<td>EIB No. 2</td>
<td>2</td>
<td>0.25</td>
<td>O.K.</td>
</tr>
<tr>
<td>IIB</td>
<td>Test in Progress</td>
<td>0.071</td>
<td>O.K.</td>
</tr>
</tbody>
</table>
Furthermore, the field tests reveal the following facts. Firstly, except for the failure of the load cells, there is no difficulty in the technique for using instrumented loading devices in the field. Secondly, the equipment (stabilized power supply, bridge circuit, and instrumented loading devices) used in this testing method is very simple and durable, and no maintenance is necessary even for long periods of field tests. Finally, except for a few occasional breakdowns, the outcome of data collection by the computer system of the power station is satisfactory.

4.5 Stability of Reference Electrode

The reference electrodes used in the high temperature SCC tests are pressure balanced external-type Ag/AgCl reference electrodes (Figure 3-25). In an attempt to check the performance of these electrodes after a long working period, a saturated calomel electrode (SCE) was used as a standard to measure each reference electrode before and after the high temperature autoclave test (Table 4-6). The results indicate that the potential value of the reference electrodes vs. the SCE gradually increased at a rate lower than 0.1 mV/hr during the test at 250 °C. The increases may be due to the dilution of the electrolyte inside the chamber during the test. In addition, potential differences were measured between different electrodes during testing. Except for a few cases, the maximum difference detected between each reference electrode was always less than 10 mV.
Table 4-6

Values of the Half Cell Potential for Pressure Balanced External Ag/AgCl/0.1M KCl Reference Electrode Used in This Study vs. SCE at Room Temperature

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Test Time (hrs.)</th>
<th>Electrode No.</th>
<th>Before the Testing</th>
<th>After the Testing</th>
<th>Difference</th>
<th>Average Drift Rate (mV/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45.2</td>
<td>90</td>
<td>44.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>43.5</td>
<td>88</td>
<td>44.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>42.6</td>
<td>broken</td>
<td>N.A.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>43.3</td>
<td>89</td>
<td>45.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>41.8</td>
<td>88</td>
<td>46.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>45.2</td>
<td>89</td>
<td>43.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>500</td>
<td>42.6</td>
<td>broken</td>
<td>0.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>530</td>
<td>41.0</td>
<td>80</td>
<td>39</td>
<td>0.091</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>42.3</td>
<td>88.2</td>
<td>47.5</td>
<td></td>
<td></td>
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<td>5</td>
<td>42.1</td>
<td>100</td>
<td>59.5</td>
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<td>88</td>
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<td>42.4</td>
<td>88</td>
<td>47.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>40.5</td>
<td>88</td>
<td>47.7</td>
<td></td>
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</tr>
<tr>
<td>4</td>
<td>42.2</td>
<td>124.5</td>
<td>82.1</td>
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</tr>
<tr>
<td>5</td>
<td>42.23</td>
<td>97.9</td>
<td>55.7</td>
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</tr>
<tr>
<td>6</td>
<td>42.4</td>
<td>89.6</td>
<td>47.6</td>
<td></td>
<td></td>
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<tr>
<td>5</td>
<td>660</td>
<td>42</td>
<td>65</td>
<td>23</td>
<td>0.068</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>750</td>
<td>42</td>
<td>65</td>
<td>23</td>
<td>0.068</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>660</td>
<td>42</td>
<td>65</td>
<td>23</td>
<td>0.068</td>
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<td>6</td>
<td>770</td>
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<td>23</td>
<td>0.068</td>
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<td>6</td>
<td>770</td>
<td>42</td>
<td>65</td>
<td>23</td>
<td>0.068</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>770</td>
<td>42</td>
<td>65</td>
<td>23</td>
<td>0.068</td>
<td></td>
</tr>
</tbody>
</table>

Note: The half cell potential of external Ag/AgCl/0.1M KCl against a saturated calomel electrode at 25°C, according to Bates's data [224], is equal to 42 mV.
during any given test. These observations confirm the fact that the reference electrodes function properly in the high temperature aqueous environment. Finally, there is a noticeable improvement in reducing the drift of the reference electrode for the 5th and 6th test (see Table 4-6). The possible reason for this improvement is that the length of the zirconia oxide at the tip of the reference electrode was doubled.

However, there was a problem related to this type of reference electrode during the tests. The alumina tube of the reference electrodes was very easy to break during the start-up stage of the experiments. The test had to be restarted whenever any one of the six electrodes broke. Recently, an unbreakable reference electrode [208] was developed in the Fontana Corrosion Center. This type of reference electrode is recommended to be used in future tests.
CHAPTER V
DISCUSSION

This chapter discusses of the data and observations presented in Chapter 4. The effects of the stress intensity, the applied potential and the degree of sensitization on the crack growth rate of the sensitized and welded specimens are discussed. The performance of the instrumented loading device and the effectiveness of the crack growth measurement technique is also evaluated.

5.1 The Effect of Stress Intensity

The results plotted in Figures 4-13 and 4-14 demonstrate that the crack growth rate of sensitized Type 304 stainless steel in high temperature sulfate solutions is dependent upon the values of $K_I$. Two regions of $K_I$ dependence can be identified. At low $K_I$ values, the crack growth rate is extremely dependent upon $K_I$, whereas at $K_I$ values greater than 20-25 MPa m$^{1/2}$, it is almost independent of $K_I$. These results generally agree with those reported by Schmidt et al. [16] for tests conducted under sustained loading in high purity water containing 8 ppm $O_2$, at 288 °C, at the open-circuit potential (see Figure 2-21).

However, the maximum crack growth rate in the plateau region measured in this study is almost one order of magnitude greater than the average value, $(7 \times 10^{-11}$ m/s),
reported by Schmidt et al. This assumes that the corrosion potential of Type 304 stainless steel in their tests is about $0 \, V_{SHE}$ [159]. A precise comparison between crack growth rates measured in both studies cannot be made because there were significant differences in the experimental conditions (temperature, potential control, DOS of the material, loading method). The agreement, nevertheless, is remarkable, taking into consideration the wide dispersion of values found when the results of different authors [16, 214-216] are compared, (see Figure 5-1) [135]. Average crack growth rates ranging from $2 \times 10^{-11} \, m/s$ to $8 \times 10^{-9} \, m/s$ have been reported at a $K_I$ value of about $20 \, MPa \, m^{1/2}$ in oxygenated high temperature water.

Schmidt et al. also found a third region in the crack velocity vs. $K_I$ plot at $K_I > 30 \, MPa \, m^{1/2}$, in which the crack growth rate increased dramatically with increasing $K_I$. A similar effect was found by Kuniya et al. [215] at slightly lower $K_I$ values (Figure 5-1), in water containing $8 \, ppm$ dissolved oxygen. This third region could not be detected in the present experiments. Specimens loaded at $K_I$ higher than $30 \, MPa \, m^{1/2}$ showed significant macrobranching, precluding precise measurements of both $K_I$ and crack growth rates, but no abrupt increase in the crack growth rate was observed. It should be noted, however, that Schmidt et al. did not find such a large increase in crack velocity for other heat-treatments and environmental conditions (288 °C
Figure 5-1 Crack growth rate data of sensitized Type 304 stainless steel collected by Andresen [135] for SCC tests conducted in 288 °C high purity water. The shaded areas refer to data scatterbands obtained by Andresen.
water with 0.2 ppm oxygen and 180 °C with 1.0 ppm oxygen) at $K_I$ ranging from 30 to 50 MPa m$^{1/2}$. Data points were plotted with large error bars in Figure 2-21, probably indicating the influence of severe macrobranching at these high $K_I$ values.

Finally, the data of the General Electric (GE) research group (EPRI Project T118-1) [217], based on the study of sensitized Type 304 stainless steel in 288 °C pure water with 8 ppm and 0.2 ppm oxygen, are superimposed on data obtained in this study to give the average crack growth rate as a function of $K_I$ (Figure 5-2). The GE data for pure water with 8 ppm and 0.2 dissolved oxygen is plotted as the upper bound and the lower bound evaluation curve, respectively. The data obtained in this study mostly lie in that bounded region. This indicates that the crack growth rates measured by the modified WOL specimen under constant load deflection agree with those measured by the compact tension specimens under a constant active load.

5.2 The Effect of Applied Potential

5.2.1 Critical Potential

The results presented in Figures 4-15 and 4-16 reveal that a critical potential for IGSCC exists, as found previously in slow strain rate tests conducted in the same solution [10, 201]. In the present study, the critical potential is between $-0.2 \ V_{\text{SHE}}$ and $-0.3 \ V_{\text{SHE}}$ for $K_I$ below about 28 MPa m$^{1/2}$; whereas the value previously measured in
Figure 5-2 Average crack growth rate data for sensitized Type 304 stainless steel showing representative evaluation curves.
the slow strain rate tests (where the strain rate was $1 \times 10^{-6} \text{m/s}$) was approximately 100 mV lower. Tsai et al. [146] have also determined a critical potential (-0.4 to -0.2 V$_{SHE}$) above which fatigue crack growth rates are significantly enhanced over those observed at lower potentials (Figure 2-31), corresponding to a change in cracking morphology from transgranular to intergranular. Their tests were conducted in the same environment, at frequencies lower than $2 \times 10^{-2}$ Hz, using a sinusoidal wave form, with $R=0.5$ and $\sigma K = 20 \text{ MPa m}^{1/2}$.

This critical potential range (0.2 to 0.3 mV$_{SHE}$) corresponds to a dissolved oxygen concentration of about 0.01 to 0.2 ppm in the elevated high purity water (274 °C) used in the tests with Type 304 stainless steel. The crack growth rate of sensitized Type 304 stainless steel in water of low oxygen concentration, as mentioned previously, is plotted as a lower bound evaluation curve in Figure 5-2. The agreement between the data obtained for the specimens tested at the low applied potential and the low oxygen concentration is very good. Therefore, this comparison confirms the point emphasized previously in Section 2.3.3.3: that the key parameter for IGSCC is the electrochemical potential, regardless of whether the source is internally dissolved oxygen or under external electronic control. As suggested by Lin [145], if the potential is lower than the critical potential, an aggressive environment can not be
built up at the crack tip, and so the crack remains arrested. On the other hand, if the potential is high enough, the metal dissolution rate will be enhanced and hydrogen ions will be produced by the hydrolysis of corrosion products (see Figure 2-35). The resulting acidic environment will enhance further dissolution as well as crack propagation. The acidification of the outlet solution observed in this test (see Figure 4-20) is strong evidence for the occurrence of hydrolysis, as suggested above.

5.2.2 Shape of Crack Front

As shown in Figures 4-8 and 4-9, the shape of the intergranular crack front depends on the applied potential at equivalent $K_I$ values. It should be noted that Schmidt et al. [16] have reported the occurrence of significant intergranular tunnelling in their fracture surfaces obtained with compact tension specimens without side-grooving, Figure 5-3(a). They suggested that crack tunnelling is the result of accelerated IGSCC, produced by a highly tri-axial state at the center of the CT specimen. On the other hand, Andresen [135] and Henry [218], using side-grooved CT specimens under similar testing conditions, have observed faster crack growth at the specimen edge than at the center (Figure 5-3(b)), and they have offered a different interpretation. While Henry [218] believes that the enhanced crack growth at the specimen edge is the consequence of a prevailing plane stress condition, Andresen [135] hypothesizes that
Figure 5-3 The shape of crack front after SCC test.  
a) Observed by Schmidt [16], and b) Observed by Andresen [135].
it is the result of occluded chemistry conditions at the crack front, which change from the center to the edge. He assumes that the diffusion path which controls the crack growth rate is shortest at the edge, thereby inducing faster crack propagation at the edges than in the center of the specimen. However, results from this present work lead to a different explanation, at least for test under potentiostatic control.

5.2.3 Mechanism for Crack Growth

It was assumed in this study two factors—mechanical and electrochemical—have an influence on the shape of the intergranular crack front. At potentials lower than 0 mV<sub>SHE</sub>, the mechanical factor associated with the dominant effect of the plane stress conditions at the edges of the modified WOL specimen enhances the crack growth rate at the edge with respect to the center, in agreement with the explanation given by Henry [218]. When the potential is increased above 0 V<sub>SHE</sub>, the electrochemical driving force for intergranular crack propagation begins to compete with the mechanical factor in the following manner.

Melville [210, 211] recently introduced an analytical model to show that in the case of a crack under potentiostatic control, an anodic current flows from both the crack tip and the crack sides. Therefore, there is a drop in potential down the crack (Figure 5-4 [210]), and this potential drop is determined by the current from the sides
Figure 5-4 Schematic representation of the potential drop proposed by Melville [211].
of the crack, the current from the crack tip, the width of the crack, and the conductivity of the solution. According to this model, when a WOL specimen is tested in the anodic potential range, it can be expected that the potential at the center of the specimen will be lower than that at the edge. Moreover, slow strain rate tests, under the same environmental conditions (Figure 2-37), indicate that a sensitized specimen is more susceptible to IGSCC, as reflected by a faster crack growth rate, when the specimen is within the potential range of -0.1 to 0.2 V<sub>SHE</sub>. On the other hand, the specimen is less susceptible to IGSCC, as reflected by a lower crack growth rate, when it is at higher anodic potentials. Hence, in the experiment carried out in this work at 0.3 V<sub>SHE</sub>, although the external potential is controlled at 0.3 V<sub>SHE</sub>, the center of the specimen may be at a lower potential. Accordingly, the intergranular crack growth may well be faster at the center than at the edges. At intermediate potentials, ranging from 0 to 0.2 V<sub>SHE</sub>, the independent effects of the mechanical and electrochemical factors cancel each other out and, therefore, the shape of the intergranular crack front follows the shape of the fatigue pre-crack.

5.2.4 Potential Drop Model

In order to support the point made previously, the following is an attempt to estimate the potential drop at the center of specimen.
According to the work of Melville, [210] if the current of the specimen is mainly generated at the tip of the crack, the potential drop within the crack may be obtained directly from Ohm's law, i.e.,

\[ V = \frac{I_0 \cdot 1}{(t \cdot w \cdot C)} \]  
Eqn. 5-1

where:

- \( I_0 \) = current at the crack tip
- \( l \) = crack length
- \( t \) = specimen thickness
- \( w \) = crack width
- \( C \) = specific conductivity of the electrolytic solution

The parameters defined above are shown schematically in Figure 5-4. As a result of this equation, a large potential drop may be obtained if there is a large current flowing from the crack tip as well as if there is a tight and long crack. Although the crack front and the counter electrode orientation used in this study (see Figure 5-5(a)), are different from those used in Melville's study, the phenomenon of the potential drop within the crack is the same. In addition, as mentioned previously (Section 4.2.4), when IGSCC occurs the crack tip of the specimen, the current is mainly generated from the tip of the crack. This condition agrees with the basic assumption of equation 5-1.
Figure 5-5 Schematic of a) current flows at the crack tip, and b) the shape of crack at the center of the cross-section of the modified WOL specimen.
As shown in Figure 5-5(a), initially the current (represented by the dotted lines) may flow almost vertically in a direction parallel to the specimen edge within the fatigue pre-crack region because this path has the highest conductance. After it reaches the machine-crack region, which is about ten times wider than the fatigue pre-crack region (see Figure 5-5(b)), the direction of the current flow will turn towards the counter electrode, and then follow a straight path from the edge of the specimen to the counter electrode. It is estimated that the longest path for the current passing through the fatigue pre-crack region is of the order of 0.5 cm, and the average width of the fatigue pre-crack is about 20 micron (Figure 5-5(b)) when the $K_I$ is 25 MPa m$^{1/2}$. The specific conductivity of the 0.01 M sodium sulfate solution at 250 °C is about 0.011 S/cm [219]. In addition, the IGSCC is assumed propagate only in a region of about 0.5 cm in width at the center of the specimen. (Note: this situation simulates the crack growth of specimen S-17, see Figure 4-8.) Hence by substituting the values above into Eqn. 5-1, it can be shown a current of about 0.01 mA is high enough to induce a voltage drop of about 400 mV at that region of the specimen.

In this study, the measured average current density is about 0.01 to 0.03 mA/cm$^2$ (corresponding to an average current of 2 to 6 mA) for specimens that have a crack growth rate higher than $10^{-10}$ m/s (see Table 4-2). As discussed
before, the current should be generated mainly from the crack tip. Therefore, a high potential drop at the center of the specimen is possible when a fast crack growth occurs in that region. However, the specific conductivity of the solution in the real crack may be higher than the value above due to the accumulation of impurities within the crack [135]. Hence, a current higher than the value calculated above, 0.1 mA is required to generate the same potential drop 300 mV.

Finally, it should be noted that the phenomenon of potential drop at the crack tip also occurs in the case of the test conducted under a controlled oxygen condition, especially in high purity water. An extra amount of electrochemical driving force (in a form of potential difference) is always required to draw the current through a tight gap from the crack tip to the specimen surface.

5.3 The Effect of Heat Treatment

5.3.1 Regular Specimen

The results plotted in Figure 4-14 indicate that the average crack growth rate of the specimen heat treated at 650 °C for 10 hours is lower than that of the specimen heat treated at the same temperature for 24 hours, especially when the tests were conducted of an applied potential of 0.2 V_SHE. The DOS study of the specimens (Figure 4-1) shows that the DOS of the specimens sensitized for 24 hours is a
little higher than that of the specimen sensitized for 10 hours, 2.3 mA/cm² and 1.8 mA/cm², respectively. A previous study by this author [82, 83] suggested that a continuous Cr-depleted zone is formed at the grain boundary as the specimen is heat treated at 650 °C for over five hours. Heating for more than five hours will only increase the width, not the depth, of the depleted zone. Therefore, it seems that a wide Cr-depleted zone enhances the IGSCC when the specimens are tested at a higher anodic potential.

5.3.2 Specimen Machined From Welded Plate

The maximum and the average crack growth rate of the W-1 specimen (Table 4-1), machined from the base metal of the welded plate, is about the same as those of the specimen machined from the Heat A material. This similarity suggests that these two materials have about the same degree of susceptibility to IGSCC. Nevertheless, the crack growth rate of W-2 (as-welded) and W-3 (as-welded + 550 °C/24 hr) specimens, which were machined from the same weld plate, is completely different from that of the W-1 specimen. One (W-2) has a zero crack growth rate, and the other (W-3) has the highest crack growth rate measured in this study. A detailed discussion of these two extreme cases follows.

5.3.2.1 As-welded Specimen

The DOS study (Figure 4-24) shows that the highest current density at 290 mV_{SHE} of the W-2 specimen is about the same as that of the Heat A specimen sensitized at 650 °C.
for about 3 to 5 hours (Figure 4-1). However, the end grain pits structures of the HAZ of the as-welded specimen after the oxalic acid test (see Figure 4-22) suggested that this high current density may be generated from some localized Cr-depleted zone within the grains or from the discontinuous Cr-depleted zone at the grain boundaries. Because the plate was not annealed before it was welded, carbide may nucleate at the localized defects inside the grain, e.g. twin boundary, inclusion, dislocation, etc. In addition, the carbide morphology nucleated at the grain boundary is a function of temperature. It tends to nucleate as small geometrical particles at high temperatures during the welding [220]. So, if the particles are far apart, the Cr-depleted zone surrounded these particles will not be continuous along the grain boundaries. Due to the reason mentioned above, the chromium depletion at the grain boundaries of the W-2 specimen was therefore not severe enough to generate continuous intergranular attack, as well as IGSCC, during the SCC test.

5.3.2.2 As-Welded Plus Post-Weld Heat Treatment

The DOS study of the W-3 specimen indicates that the heat treatment after welding did not dramatically increase the DOS of both the HAZ and the base metal of the specimen (Figure 4-23). However, it is noted that, during the heat treatment, due to the diffusion rate of chromium, chromium depletion at the grain boundaries is more severe than at the
other localized defects (twin grain boundary, dislocation). Hence, the increase in the current density of the specimen, after heat treatment, should be mainly induced by the Cr-depleted zone along the grain boundaries. The result of the oxalic acid test confirm this analysis. A continuous ditch structure was observed at the HAZ of the as-welded plus post-weld heat treatment specimen (see Figure 4-22).

In addition, according to the STEM work of Ruther et al. [101] and the calculation from this authos's previous work [82], the width of the depleted zone of the W-3 specimen should be narrower than that of the W-1 specimen by about one-third. Consequently, the average current density from the depleted zone of the W-3 specimen should be higher than that from the depleted zone of the W-1 specimen. Furthermore, since the current density of the DOS study is a function of the chromium content of the alloy (Figure 5-6) [83], the depletion profile of the W-3 specimen, as shown in Figure 5-7, should deeper than that of the W-1 specimen. The result of above analysis agrees with the work of Tedmon [221], and Strawstrom and Hillert [222]. They claimed that the minimum chromium content of the depleted zone is a strong function of the heat treatment temperature, namely, the minimum chromium content of the depleted zone increase as temperature increases.

The manner in which the minimum chromium content near the grain boundaries effects the crack growth rate could be
Figure 5-6 Current Density at 290 mV$_{SHE}$ on anodic polarization curves in 1 N HClO$_4$ + 0.2 N NaCl as a function of chromium content of Fe-Cr alloy.
Figure 5-7 Schematic of chromium profile across the depleted grain boundaries of furnaced sensitized specimen and as-welded plus post-weld heat treatment specimen.
examined on the reaction surface (Figure 2-12) introduced by Ford [80]. As mentioned in Section 2.2.2, the crack growth rate depends on the oxide rupture rate, passivation rate, and liquid diffusion rate. According to the work of Indig and McIlree [159], the passivation rate of the Fe-Ni-Cr alloy in a deaerated dilute sodium sulfate solution at 288 °C under an applied potential 0 mV SHE decreases as the chromium content decreases. On the reaction surface (Figure 2-12), the effect of the passivation rate is represented by the response vector (a), which predicts that the crack growth rate increases as the passivation rate decreases. In this study, since the passivation rate at the depleted grain boundaries of the W-3 specimen is lower than that of the W-1 specimen, the W-3 specimen should have a higher crack growth rate than that of the W-1 specimen during the SCC test.

5.4 Evaluation of The Instrumented Loading Devices

From the experimental results revealed in section 4.4.4, it is apparent that the IIB is the only loading device that could function properly when tested under conditions simulating BWR environmental conditions, namely, a 0.01 N sodium sulfate solution, at 5.2 MPa (750 psi), and under an applied potential. The data plotted in Figure 4-17 clearly demonstrate that using this device with the load relaxation method allows the crack growth rates to be deter-
mined with relative accuracy. The success of this loading device is based on the following:

1) It is instrumented with a higher quality weldable strain gage (Ailtech SG 424 platinum-tungsten strain gage), which is stable at the operating temperature.

2) Its design is very delicate. The embedded strain gage can not only sense the load variation linearly and precisely, but can also avoid any environmental damage.

3) It is made of Inconel X-750 alloy, which has very good corrosion resistance in the operating environment.

The load cell and EIB do not function properly under the same testing environment. The main difficulties are as follows:

1) Stress corrosion cracking close to the weld junction in the load chamber (made of 17-4 PH stainless steel) of the load cells resulted in the entry of water which caused a deterioration in the instrumented strain gages.

2) The load signal was drifting significantly, especially for EIB, at the operating temperature during the test. This drift was mainly caused by the instability of the instrumented strain gages (made of a chromium-nickel alloy).

On the other hand, the field test results in Section 4.4.5 reveal that, except for the failure of the load cells after long service, the devices developed in this study function properly in an actual power plant steam environment.
(150 °C, 0.2% moisture). However, due to minor load signal drift (Figure 4-34), the load cell and IIB are not suitable for monitoring the crack growth rate of the specimen when the crack growth rate of the specimen is lower than $10^{-10}$ m/s. Therefore, under this situation, the IIB is still the only device that can yield accurate data for the specimen which has a low crack growth rate. The field test also reveals another advantage for the IIB. Because of the autoclave is small, only 4 specimens loaded with load cells can be accommodated, while 15 specimens with the IIB can be installed.

Finally, the price of these loading devices is about the same. Each load cell, EIB, and IIB costs $1,200, $900, and $950, respectively.

5.5 Evaluation of the Crack Growth Measurement Technique

As mentioned before in the Introduction, one of the major advantages for the testing method developed in this study is that the complete $da/dt$ vs. $f(K_i)$ curve as well as the $K_{ISC}$ of the material can be determined by using a single specimen. Except this, there are several other advantages for this test method and these are described below.

The loading mechanism of the specimen is very simple; it is self-stressed by an instrumented loading device. Unlike the compact tension specimen or dead weight-loaded cantilever-beam specimen, a loading machine or a large
testing texture is necessary to load the specimen. In addition, the size of the IIB, the instrumented loading device developed in this study, is very compact; it has the same physical size as a regular bolt. Therefore, several specimens can be tested simultaneously in a small autoclave.

Furthermore, because the equipment for conducting the tests and for collecting the data are very simple and inexpensive, and are capable of testing in the field for long periods, this testing method can be used extensively in the field to study the crack growth rate of the different materials in different field environments.

Finally, the developed testing method can be used on other types of specimens, for example, constant deflection specimens. According to the calculation made by Hoagland [223], it is possible to develop a type of fracture mechanics specimen which has a constant $K_I$ value when it is loaded under constant deflection conditions. The crack growth rate of the specimen can be measured by the load relaxation method, as mentioned in Section 3.5, when the compliance curve of the specimen is obtained. The advantage for using this type of specimen is that one can study how the environmental factors affect the crack growth rate of the specimen under a constant $K_I$ value.

However, there are several disadvantages with this testing method. Firstly, it can not be used in environments which can cause extensive corrosion of the loading device
itself. Secondly, the loading devices need to be calibrated very carefully. Finally, calculation of the data obtained from this method is complicated.
6.1 SCC Testing

The important findings of the SCC test of Type 304 stainless steel in 0.01 M sodium sulfate solutions at 250 °C under an applied potential are:

1. Furnace sensitized Type 304 stainless steel, in the form of modified 1-T (1" thick) WOL specimens, exhibited intergranular crack propagation in a deaerated or air-saturated 0.01 m sodium sulfate solution within a potential range from -0.2 V_{SHE} to 0.3 V_{SHE} at initial $K_I$ values of between 17 to 42 MPa m$^{1/2}$.

2. A critical potential for the propagation of intergranular cracks, was measured to be about -0.25 V_{SHE}. Above this potential, the crack growth rate increased with increasing potential, and attained a maximum value at about 0 V_{SHE}.

3. The intergranular crack growth rate of the furnace sensitized specimen was found to be strongly dependent upon $K_I$ for $K_I$ values below about 20 to 25 MPa m$^{1/2}$. At $K_I$ values above that range, maximum crack growth rates of about $1 \times 10^{-9}$ m/s were measured at 0 V_{SHE}.

4. The value of the applied potential has an important influence on the shape of the intergranular crack front.
While at low potentials (-0.2 to 0 SHE) crack rates were faster at the edges than in the center of the specimen, the opposite was found at high anodic potentials (0.3 V_{SHE}). A model based on a potential drop down a tight crack is adopted to explain this phenomenon.

5. Post-welding heat-treatment has an important effect on the crack growth rate of the welded specimens. While the as-welded specimen did not show detectable crack growth at a potential of 0 V_{SHE}, a specimen heat treated for 24 hours at 550 °C after welding had a maximum crack growth rate of 3.8 \times 10^{-9} \text{ m/s}. The minium chromium content at the Cr-depleted zone near the grain boundaries plays an important role in affecting the crack growth rate.

6. When the furnaced sensitized specimen tested at a potential higher than about 0.1 V_{SHE}, the heat-treatment time at 650 °C has an important effect on the crack growth rate of the specimen. Under the applied potential of 0.2 V_{SHE}, specimens sensitized for 24 hours had a crack growth rate about five times higher than that of the specimens sensitized for 12 hours.

7. The open circuit potential for sensitized Type 304 stainless steel in an aerated 0.01 m sodium sulfate solution at 250 °C was about 0.06 V_{SHE}, but dropped to about -0.71 V_{SHE} in the deaerated solution.

8. Applied stress intensities of the specimen higher than 30 MPa m^{1/2} produced intergranular macrobranching. In
order to apply the elastic fracture mechanics analysis technique to the test results, an initial applied stress intensity below that value is required.

9. The design of the circulating autoclave system and the arrangement of the electrodes allow a potentiostatic control for multi-specimen tests.

10. The Ag/Ag/Cl/0.1 M KCl pressure balanced external reference electrode performed satisfactorily at 250 °C for over 700 hours.

6.2 Loading Devices

The experiences and the important accomplishments in developing instrumented loading devices and the techniques to measure the crack growth rate of the 1-T modified WOL specimen in-situ are:

1. An internal instrumented bolt (IIB), which is made of Inconel X750 alloy and instrumented with the Pt-W type strain gage, was found to be an inexpensive, compact, and reliable device for monitoring load relaxation during crack propagation in high temperature/high pressure aqueous environments.

2. With the equipment used in this study, the sensitivity of the IIB is adequate to measure the crack growth rate of the specimen in the order of $10^{-11}$ m/s.

3. The load relaxation technique developed in this study is adequate for measuring the crack growth rate of a multi-specimen system for a long-term field test.
4. The loading devices made by Cr-Ni type strain gages were not stable enough to measure the slow crack growth rate \(10^{-10} \text{ m/s}\) of the specimen at 250 °C.

5. Type 17-4 PH stainless steel is not a suitable material for manufacturing loading devices used in high temperature dilute sodium sulfate solutions. It is susceptible to SCC in that environment.
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CALCULATE CRACK LENGTH OF WOL SPECIMEN

WHEN WE KNOW THE COD AND LOAD P

PRINT

INPUT CONSTANT

E, B, COD AND LOAD

INPUT "YOUNG'S MODULUS (X10^-6) = " ; E1 : PRINT : LET E=E1*10^-6

INPUT "SPECIMEN THICKNESS = " ; B : PRINT

INPUT "COD (MV) = " ; V1 : PRINT : V=V1*10^-3*4.074

INPUT "LOAD (LBS) = " ; P : PRINT

REM CALCULATE C6

LET A=.77

LET N=1

LET D1=3.453

LET D2=8.097

LET D3=42.314

LET D4=64.677

LET D5=36.845

LET D0 = A/2.55

LET C6=EXP(D1-D2*D0+D3*D0^2-D4*D0^3+D5*D0^4)

LET PT = E*B*V/C6

SET A DO LOOP TO FIND A

CORRECT CRACK LENGTH

IF ABS(PT - P) < 1 GOTO 340

LET A=A-(-.1)^N

DO=A/2.55

IF (P-PT)*(-1)^N>0 GOTO 220

N=N+1

GOTO 280

PRINT "CRACK LENGTH = " ; A

INPUT "DO YOU WANT CALCULATE ANOTHER LOAD ? "; A#

IF A#="Y" GOTO 100

END
APPENDIX B

LINEAR LEAST-SQUARE FIT -- MAY 26, 1983

BY PAUL CHUNG

THIS PROGRAM CAN DO FOLLOWING THINGS
1. PLOT LEAST-SQUARES FIT CURVE ON SCREEN OR ON EPSON PRINTER
2. CALCULATE CORRELATION COEFFICIENT
3. CAN OPEN EITHER RANDOM DATA FILE OR SEQUENTIAL DATA FILE

F2: FUDGE FACTOR
L3: NUMBER OF PLOT LINES
M1: MAXIMUM LENGTH
N1: ROW NUMBER
Y1: YCALC: CALCULATED Y
C3: CORREL: CORRELATION COEFFICIENT
E2: SIGMAA ERROR ON A
SIGMAB ERROR ON B

INPUT "NUMBER OF STRING SPACE = (200) " ; Cl
CLEAR Cl
A$ = "### #### ##########
C$ = "##.####
INPUT "MAXIMUM LENGTH = (35) M1"
DIM X(M1), Y(M1), Y2(M1)
REM
PRINT I I
PRINT HOW YOU WANT TO GET THE DATA ?
PRINT "1. INPUT A RANDOM DATA FILE FROM KEY BOARD"
PRINT "2. CALL A RANDOM DATA FILE FROM DISKETTE"
PRINT "3. CALL A SEQUENTIAL DATA FILE FROM DISKET.";
PRINT "4. END"
INPUT Cl
IF Cl=4 GOTO 9999
INPUT "FILE NAME": N1*
INPUT "REMARK": N2*
ON Cl GOTO 610, 650, 720, 9999
INPUT "STARTING POINT": ; T11: INPUT "ENDING POINT": ; N1
FOR I1=T11 TO N1
PRINT II,
INPUT "X = ": ; X(I1) ; INPUT " Y = ": ; Y(I1)
IF Y(I1)=-1 GOTO 625
END
INPUT "X SPACE FOR THE PLOTTING: "; II
L3=II*(N1-T11)+1
RETURN
REM GO TO RANDOM DATA GET SUBROUTINE
GOSUB 730
PRINT
GOSUB 870
GOTO 725
REM GO TO SEQUENTIAL DATA GET SUBROUTINE
GOSUB 920
RETURN
FILES : PRINT: PRINT
INPUT "DATA FILE NAME: "; NF*: PRINT
INPUT "FIELD LENGTH= ";F1
OPEN "R", 2, NF*,F1 : PRINT
INPUT "NO. OF VARIABLE = "; N: PRINT
LET FL = 1
IF FL > N GOTO 820
PRINT "FIELD LENGTH OF NO. "; FL; " VARIABLE";
INPUT D(FL): PRINT
LET FL = FL + 1
GOTO 790
ON N GOTO B25, 830, 835, 840, 845, 850, 855, 860
FIELD 2, D(1) AS D$(1) ; GOTO B65
FIELD 2, D(1) AS D$(1), D(2) AS D$(2): GOTO B65
FIELD 2, D(1) AS D$(1), D(2) AS D$(2), D(3) AS D$(3): GOTO B65
FIELD 2, D(1) AS D$(1), D(2) AS D$(2), D(3) AS D$(3), D(4) AS D$(4): GOTO B65
FIELD 2, D(1) AS D$(1), D(2) AS D$(2), D(3) AS D$(3), D(4) AS D$(4), D(5) AS D$(5): GOTO B65
RETURN
INPUT "NO. OF VARIABLE YOU WANT TO PLOT : "; NV: PRINT
LET T11=TI
GET 2 ,T1
LET VM = VAL(D$(NV))
LET Y(T1)= INT(VM#1000+.5)/1000: X(T1)=T1
T1=T1+1
IF T1>N1  GOTO 913
GOTO 885
LET TI=T1
GOTO 2,T1
LET VM = VAL(D$(NV))
INPUT Y(T1)= INT(VM*1000+).5)/1000: X(T1)=T1
T1=T1+1
IF T1>N1 GOTO 913
GOTO 885
L3=N1-T11+1
RETURN
OPEN A SEQ. FILE 
INPUT "WHICH DISKET DRIVER YOU WANT? (A OR B)"; W#
FILES "B:": PRINT: PRINT: GOTO 945
FILES : PRINT: PRINT
INPUT "DATA FILE NAME: "; NS#
INPUT "START TIME = "; T1
INPUT "END TIME = "; N1
OPEN "I", W2, NS#
FOR SI = 1 TO N1
LET Y(S1)=INT(VM*1000+.5)/1000
LET X(S1)=S1
980 PRINT X(SI), Y(SI)
985 NEXT SI
990 CLOSE #2
993 L3=N1-T11+1
995 RETURN

1000  PRINT RESULTS
1001  PRINT: PRINT
1002 PRINT "HOW TO SHOW THE DATA? 1 - SCREEN"
1003 PRINT "  2 - PRINTER"
1004 INPUT 13
1005 ON 13 GOTO 2000, 1006
1006 LPRINT CHR*(27) "2" CHR*(18)
1008 LPRINT "NAME OF THE DATA FILE: " ; N1$
1009 LPRINT "REMARK: " ; N2$: LPRINT ""
1010 LPRINT "  X  Y  Y CALC"; LPRINT ""
1011 FOR I=T11 TO N1
1013 LPRINT USING A$; I; X(I), Y(I), Y2(I)
1014 NEXT I
1015 LPRINT
1016 LPRINT "COEFFICIENTS"
1017 LPRINT "  INTERCEPT IS " ; A; "SIGMA IS" ; E2
1018 LPRINT "  SLOP IS " ; B; "SIGMA IS" ; E3
1019 LPRINT
1020 LPRINT "CORRELATION COEFFICIENT IS " ; C3
1021 RETURN: REM FROM PRINTOUT

2000  PRINT RESULTS
2010 PRINT "  X  Y  Y CALC"
2020 FOR I=1 TO N1
2022 PRINT USING A$; I; X(I), Y(I), Y2(I)
2023 NEXT I
2025 PRINT
2030 PRINT "COEFFICIENTS"
2037 PRINT "  INTERCEPT IS " ; A; "SIGMA IS" ; E2
2038 PRINT "  SLOP IS " ; B; "SIGMA IS" ; E3
2039 PRINT
2100 PRINT "CORRELATION COEFFICIENT IS " ; C3
2110 RETURN: REM FROM PRINTOUT

5000  FIT A STRAIGHT LINE THROUGH Y VS X, MAY 26, 1983
5020
5030 S3=0 ; S7=0
5040 S4=0 ; S9=0
5050 S9=0
5060 FOR K=T11 TO N1
5070 X=X(K)
5080 Y=Y(K)
5090 S3=S3+X
5100 S7=S7+Y
5110 S9=S9+X*Y
5120 S4=S4+X*X
5130 S8=S8+Y*Y
5140 NEXT K
5145 LET N11=N1-T11+1
5150 T2=S4-S3*S3/N11
5160 T3=S7-S3*S7/N11
5170 T4=S8-S7*S7/N11
5180 B=T3/T2
5190 A=((S4*S7-S3*S9)/N11)/T2
5200 C3=T3/SQR(T2^T4)
5205 IF (S8-A*S7-B*S9)<0 GOTO 5235
5210 T5=SQR((S6-A*S7-B*S9)/(N11-2))
5220 E3=T5/SQR(T2)
5225 E2=E3*SQR(S4/N11):GOTO 5240
5230 E3=-1 : E2 = -1
5240 FOR K=T11 TO N1
297

5250 \( Y_2(k) = A + B \cdot X(k) \)
5260 NEXT \( K \)
5270 RETURN; REM FROM LEAST SQUARES FIT
7000 REM PLOT Y AND Y2 AS FUNCTION OF X, MAY 26, 1983
7001 PRINT: PRINT: PRINT "HOW TO SHOW THE PLOT? 1 - SCREEN"
7002 PRINT " 2 - PRINTER"
7003 PRINT: PRINT: PRINT "NEXT K"
7004 ON I2 GOTO 8000, 7010
7005 LPRINT CHR$(15)
7006 LPRINT CHR$(27) "1"
7007 LPRINT: LPRINT: LPRINT
7008 FOR J = 1 TO 11
298

7390 GOSUB 7820
7400 GOTO 7470
7410 K2=FNK4(Y(L))
7420 L4(K2) = 1
7430 K2=FNK4(Y2(L))
7440 L4(K2)=2
7450 GOTO 7370
7460 LPRINT "-"; TAB(119); "-"
7470 IF((X(L)-(X5+X6*.5))>W2<=0)THEN 7500
7480 J4=1
7490 GOTO 7560
7500 J4 = 0
7510 K2 = FNK4(Y(L))
7520 L4(K2)=1
7530 K2 = FNK4(Y2(L))
7540 L4(K2)=2
7550 X2=X5.
7560 NEXT I
7570 IF(L>=N1) THEN 7640
7580 L = L + 1
7590 K2 = FNK4(Y(L))
7600 L4(K2) = 1
7610 K2 = FNK4(Y2(L))
7620 L4(K2)=2
7630 GOTO 7570
7640 GOSUB 7820
7650 Y6=Y5*10
7660 V2(J+1)=Y4
7670 FOR J = 1 TO 9
7680 V2(J+1)=V2(J)+Y6
7690 NEXT J
7700 V2(11)=Y3
7710 LPRINT P3$; ";
7720 FOR J=1 TO 11
7730 LPRINT B$;
7740 NEXT J
7750 LPRINT ";"; LPRINT
7760 LPRINT " ";
7770 FOR J = 1 TO 11
7780 LPRINT USING B1$; V2(J); V2(J+1);
7790 NEXT J
7800 LPRINT
7810 RETURN
7820 FOR J = 101 TO 1 STEP -1
7830 IF(L4(J)) THEN 7870
7840 NEXT J
7850 LPRINT
7860 RETURN
7870 J5 = J
7880 L$=" ";
7890 FOR J = 1 TO J5
7900 IF (L4(J)=0) THEN L$ = L$ + " ";
7910 IF (L4(J)=1) THEN L$ = L$ + "*"
7920 IF (L4(J)=2) THEN L$=L$ + "+
7930 NEXT J
7940 IF II>2 GOTO 7940
7950 IF (X2/5-INT(X2/5))<.1 GOTO 7940
7960 LPRINT " "; L$; TAB(119);
7970 FOR J = 1 TO L6
7980 L4(J)=0
7990 NEXT J
8000 ' ARRAYS L4 AND V2 ARE DIMENSIONED AT THIS POINT
B010 L6 = 51 : B* = "^" : REM PLOT ' Y SCALE
B020 B$="####.###" : P3$="  
B030 PRINT: PRINT: PRINT
B040 IF (L3<3) THEN L3 = 15: REM DEFAULT PLOT LENGTH
B050 IF (N4) THEN B090
B060 N4 = 1
B070 DIM L4(S1), V2(6)
B080 DEF FNX4(P)=(P-Y4)/Y5 +1
B090 X4 = X(1)
B100 X3 = X(N1)
B110 Y4 = Y(1)
B120 Y3 = Y4
B130 X6 = (X3-X4)/(L3-1)
B140 IF (X6 > 0) THEN W2 = 1
B150 IF (X6<0) THEN W2 = -1
B160 FOR I = 1 TO N1
B170 IF (Y(I)<Y4) THEN Y4 = Y(I)
B180 IF (Y(I)>Y4) THEN Y4 = Y2(I)
B190 IF (Y(I)>Y3) THEN Y3 = Y(I)
B200 IF (Y(I)<Y3) THEN Y3 = Y2(I)
B210 NEXT I
B220 Y5 = (Y3-Y4)/(L6-1)
B230 FOR I = 1 TO L6
B240 L4(I) = 0
B250 NEXT I
B260 X2 = X4
B270 J4 = 0
B280 L=1
B290 K2 = FNX4(Y(1))
B300 L4(K2)=1
B310 K2 = FNX4(Y2(1))
B320 L4(K2)=2
B330 FOR I = 2 TO L3
B340 X5=X4+X6*(I-1)
B350 IF (J4=1) THEN B450
B360 L=L+1
B370 IF((X(L)-(X5-X6*.5))*W2<=0)THEN B400
B380 GOSUB BB10
B390 GOTO B460
B400 K2=FNX4(Y(L))
B410 L4(K2) = 1
B420 K2=FNX4(Y2(L))
B430 L4(K2)=2
B440 GOTO B360
B450 PRINT " -"
B460 IF((X(L)-(X5+X6*.5))*W2<=0)THEN B490
B470 J4=1
B480 GOTO B550
B490 J4 = 0
B500 K2 = FNX4(Y(L))
B510 L4(K2)=1
B520 K2 = FNX4(Y2(L))
B530 L4(K2)=2
B540 X2=X5
B550 NEXT I
B560 IF(L>=N1) THEN B630
B570 L = L + 1
B580 K2 = FNX4(Y(L))
B590 L4(K2) = 1
B600 K2 = FNX4(Y2(L))
B610 L4(K2) = 2
B620 GOTO B560
B630 GOSUB BB10
B640 Y6=Y5*10
B650 V2(I) = Y4
B660 FOR J = 1 TO 4
8670  V2(J+1)=V2(J)+Y6
8680  NEXT J
8690  V2(6) = Y3
8700  PRINT P3$; " ";
8710  FOR J=1 TO 6
8720  PRINT B$;
8730  NEXT J
8740  PRINT " ";
8750  PRINT " ";
8760  FOR J = 1 TO 6
8770  PRINT USING B1$; V2(J);;
8780  NEXT J
8790  PRINT
8800  RETURN
8810  FOR J = 51 TO 1 STEP -1
8820  IF(L4(J)) THEN 8860
8830  NEXT J
8840  PRINT
8850  PRINT "TYPE <CONT> TO CONTINUE THE PROGRAM"; STOP
8860  RETURN
8870  J5 = J
8880  FOR J = 1 TO J5
8890  IF (L4(J)=0) THEN L$ = L$ + " 
8900  IF (L4(J)=1) THEN L$ = L$ + "+"
8910  IF (L4(J)=2) THEN L$=L$ + "#
8920  NEXT J
8930  PRINT X2; P3$; L$;
8940  FOR J = 1 TO L6
8950  LA(J)=0
8960  NEXT J
8970  L$=""
8980  RETURN : REM END OF PLOT
9999  LPRINT CHR$(27) "2" CHR$(18)