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Mozhi, T. Arul

THE EFFECT OF NITROGEN ON SENSITIZATION AND STRESS CORROSION CRACKING OF AISI 304 STAINLESS STEELS

The Ohio State University

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THE EFFECT OF NITROGEN ON SENSITIZATION AND STRESS CORROSION CRACKING OF AISI 304 STAINLESS STEELS.

DISSERTATION

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

By

T. Arul Mozhi, B. Tech., M.S.

* * * * * * *

The Ohio State University
1986

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Mozhi, K. Nishimoto, B.E. Wilde and W.A.T. Clark, Corrosion (in
Press).

"Thermodynamic Modeling of Sensitization in AISI 304 Stainless
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Jagannathan, B.E. Wilde and W.A.T. Clark, Scipta Metal1. (to be
Submitted)

"Electroconduclting glass fibers produced by ion-exchange and
reduction treatments", by T.A. Mozhi and D. Chakravorty, Journal of

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Cracking of Type 304 Stainless Steels", by T. A. Mozhi, W.A.T. Clark
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- IGSCC at \(-0.1 \, V_H\).
- Secondary cracks at \(-0.1 \, V_H\).
- IGSCC at \(0 \, V_H\).
- Pitting at \(0'V_H\).

SEM fractographs for B-8 stainless steel.

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- IGSCC at \(-0.2 \, V_H\).
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CHAPTER I
INTRODUCTION

Sensitization is the enhanced susceptibility of stainless steels to intergranular corrosion (IGC) (i.e., localized attack at and adjacent to grain boundaries, with relatively little corrosion of the grains) following heat treatment in the temperature range of 500 to 850°C. Stress corrosion cracking (SCC) is the cracking caused by simultaneous presence of a tensile stress and a specific corrosive environment. Sensitization in the heat affected zones (HAZ) of AISI 304 stainless steel (SS) welded piping used in boiling water reactors (BWRs) has caused serious intergranular stress corrosion cracking (IGSCC) failures during the past decade. While these failures have not constituted a hazard to the public, they have cost power utility companies several billions of dollars for replacement power and repairs; for example, the loss of 1000 Megawatts of nuclear power during an outage costs one million dollars a day, replacement of the cracked primary piping system in the Nine Mile Point BWR cost 150 million dollars.

To avoid IGSCC failure of BWR piping in the future it is first necessary to identify the required conditions for cracking and then control them. There are three required conditions for IGSCC: 1) a sensitized microstructure, 2) specific environmental conditions and 3) a critical level of stress. All three required conditions are present in the BWR piping as listed below. The sensitized microstructure is
produced in the HAZ formed during welding. The environmental condition is fulfilled due to the presence of the dissolved oxygen generated by the radiolysis of water at the normal BWR operating condition, which increases the corrosion potential above the critical potential for IGSCC. The stresses responsible for the cracking 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. The first condition, the sensitized microstructure, can be controlled by reducing the carbon content of the stainless steel and hence retarding sensitization; but the mechanical properties of the stainless steel would be degraded if the carbon content is low, so nitrogen is added to improve the strength (5). The effect of nitrogen and carbon on sensitization of AISI 304 SS must be understood. The second condition, the specific environmental conditions, can be controlled by maintaining the corrosion potential of the stainless steel below the critical potential for IGSCC (6). The effect of nitrogen, carbon and potential on SCC of AISI 304 SS in simulated BWR environments must be understood. The third condition, the critical level of stress, was not investigated in this study.

There are some investigations on the effect of nitrogen on sensitization of stainless steels which indicate that nitrogen additions retard sensitization of (7-9), but the mechanisms involved in it, and the relationship between sensitization and susceptibility to SCC in BWR environments, have not yet been fully understood. There are many investigations on the effect of nitrogen on SCC of austenitic stainless steels, but these have focussed on transgranular stress
corrosion cracking (TGSCC) that occur in boiling MgCl₂ solutions (10-21), which indicate that nitrogen is detrimental to SCC resistance even at levels as low as 0.03 wt.%; and although there are numerous investigations which have concentrated on IGSCC of sensitized austenitic stainless steel in BWR environments (22-34) none of these have investigated the effect of nitrogen on SCC, in spite of the fact that new grades of austenitic stainless steels with carbon levels reduced to prevent IGC and with nitrogen additions to improve strength have been proposed as alternative materials for BWR piping (5, 35-39). So it is of great scientific and engineering importance to carry out a systematic investigation using alloys with controlled nitrogen and carbon levels in order to study the effect of nitrogen on sensitization and SCC of AISI 304 SS.

The aim of this investigation was 1) to study alloys which had a systematic and controlled variation of both nitrogen and carbon, 2) to investigate the effect of nitrogen and carbon on sensitization by theoretical modeling and experimental verification by using electrochemical and electron-optical techniques, and 3) to investigate the effect of nitrogen, carbon and electrode potential on SCC susceptibility, using electrochemical and mechanical tests, carried out under controlled electrochemical and mechanical conditions, in simulated BWR environments, and subsequent electron-optical examination of the fracture surface and dislocation structure. These studies should help to understand how control of the sensitized microstructure (and microchemistry, because both the extent of chromium carbide precipitation and the associated chromium depletion are involved in
sensitization) and specific environmental conditions (the most important being electrochemical parameters) can prevent IGSCC failure of BWR piping in the future. To achieve this aim it was necessary:

1. To analyze the sensitization of AISI 304 SS based on theoretical models and predict the effect of nitrogen on it; for this purpose computations were performed based on: 1) thermodynamic models to construct time-temperature-sensitization (TTS) diagrams and to calculate the chromium concentration at the carbide-austenite interface \(X_{C_r}^i\), and 2) kinetic models to calculate the chromium concentration profiles in the vicinity of chromium carbides precipitated at the grain boundaries.

2. To compare the predictions based on the theoretical models of the effect of nitrogen on sensitization of AISI 304 SS to the experimental results obtained using both the electrochemical technique: electrochemical potentiokinetic reactivation (EPR) tests and the electron-optical technique: analytical electron microscopic (AEM) studies, taking into consideration the effect of the electron beam broadening on the AEM measurements.

3. To study the anodic polarization behavior of AISI 304 SS containing nitrogen which would help to predict or explain its SCC performance in simulated BWR environments, using electrochemical techniques.

4. To study the SCC susceptibility of AISI 304 SS containing nitrogen in both high temperature deaerated aqueous sulphate
and chloride solution, at various applied potentials and strain rates, using the slow strain rate tests (SSRTs); and examining the fracture and side surfaces of the SSRT specimens using the scanning electron microscope (SEM) to determine the:

1) mode of failure - IGSCC, TGSCC or ductile, and
2) occurrence of pitting and secondary cracks.

5. To correlate the: 1) theoretical calculations, EPR and AEM results which indicate the extent of sensitization, and 2) anodic polarization behavior and applied potential in the SSRT which are the relevant electrochemical conditions, to the occurrence of IGSCC in simulated BWR environments.

The following chapters in this dissertation describe how the problem of IGSCC of BWR piping was investigated systematically to come up with new grades of AISI 304 SS with low carbon and with nitrogen additions which are resistant to IGSCC in BWR environments; Chapter 2 contains the literature search which provides the necessary background information, Chapter 3 describes the theoretical modeling of sensitization, Chapter 4 describes the materials and experimental procedures used in this investigation, Chapter 5 presents the results and analysis in an organized manner, Chapter 6 contains the discussion of the results and the analysis in a logical sequence and, Chapter 7 gives the summary and conclusions of this investigation and suggestions for future work.
2.1 Sensitization and IGSCC of BWR Piping

There have been as many as 380 incidents of IGSCC failures of sensitized AISI 304 SS BWR piping, but none of them has caused pipe severance nor do they constitute a safety issue. The position of the power utility industry and the Nuclear Regulatory Commission is the "leak-before-break" concept, i.e. a leak will occur before the tough ductile AISI 304 SS will experience a complete separation (3). However pipe cracking has created serious problems of plant availability, radiation exposure of skilled personnel, and huge expenses for inspection and repair operations, to power utility companies.

A brief description of the BWR and the primary BWR environment is given below, to give the necessary background for understanding the problem of sensitization and IGSCC of BWR piping.

2.1.1 The Boiling Water Reactor

Roberts has given a detailed description of the BWR (40), from which the following material is presented. The BWR uses the steam cycle conversion system like that in fossil fuel power plants, and the steam produced from water circulated through the reactor core by nuclear heat, drives a conventional turbine generator to produce electricity.
schematic of the BWR is shown in Figure 1 (40). It consists of a nuclear core assembled within a pressure vessel and necessary auxiliary systems for safeguards, control, and instrumentation. The saturated steam that is generated by nuclear heat from the reactor core, is separated from recirculation water, dried in the top of the vessel, and directed to the turbine generator through large 304 stainless steel steam lines at 1000 psi and 288°C, and the condensed steam is recirculated to the reactor.

2.1.2 The Primary BWR Environment

The primary BWR environment is high purity water, which has a conductivity < 1 μS/cm and a chloride concentration < 0.2 mg/L. It is circulated through the reactor cycle, and can either be characterized by combinations of temperature and chemical species or by combinations of temperature and electrochemical potentials (ECP) that occur (41). The primary chemical species are dissolved gases like oxygen, hydrogen, and hydrogen peroxide produced, as a result of radiolysis of water in the reactor core. During the steady state at 288°C, the oxygen is between 30 and 350 parts per billion (ppb) and hydrogen is between 15 and 30 ppb, while hydrogen peroxide is zero because it decomposes at 170°C. In actual practice the primary BWR environment also contains small impurities, such as chloride and sulfate ions at the ppb level (41). In the present investigation SCC tests were conducted in high temperature aqueous sulfate and chloride environments. The combinations of temperature and ECP that occurs in the BWRs are shown in Figure 2 (41). It is seen that the value of ECP is approximately 0.2 to 0.5 V_H at start-up and gradually decreases to about 0 to -0.3 V_H during steady
Figure 1 Schematic diagram of the BWR (40)
Figure 2  Variation of ECP with temperature during startups and steady states of several BWRs (41)
state. ECP is a measurement that accounts for all the chemical species present and may be thought to represent the driving force for IGSCC, but it is not a thermodynamic quantity because the electrochemical systems may not be in equilibrium (41). In the present investigation ECP is an important variable in the SCC tests.

2.2 **Sensitization of Austenitic Stainless Steels**

Austenitic stainless steels have excellent resistance to general corrosion in a variety of aggressive environments. This is attributed to the presence of greater than 11-12 wt.% of chromium, which forms a passive film on the surface. But they suffer from severe localized corrosion phenomena like IGC, SCC, etc.

IGC is the localized attack at and adjacent to grain boundaries, with relatively little corrosion of the grains (1). Grain boundaries are disordered misfit regions separating grains of different crystallographic orientation, and hence they are favored sites for the segregation of various solute elements or the precipitation of metal compounds, such as carbides, and sigma phases; and therefore in certain corrosive environments grain boundaries are preferentially attacked (42). In stainless steels, IGC as a result of segregation of certain solute elements to grain boundaries, occurs only in highly oxidizing corrosive containing cations in high valence states such as Cr\(^{+6}\). This is generally not encountered in service, the usually encountered form of IGC is due to sensitization. Sensitization is the enhanced susceptibility of stainless steels to IGC following heat treatment in the temperature range of 500 to 850°C (1).
2.2.1 Characteristics of Sensitization

The following observations are typical characteristics of the sensitization phenomenon in austenitic stainless steels (43):

1. Quenching through the temperature range 500 to 850°C does not result in sensitization, provided the cross section of the specimen is sufficiently small and the quench rates are uniformly rapid throughout the specimen.

2. Quenching from an elevated temperature followed by reheating into the temperature range 500 to 850°C results in sensitization, with the degree of sensitization (DOS) being dependent on the sensitizing temperature and time, and alloy composition.

3. TTS diagrams of austenitic stainless steels exhibit a C-curve behavior with the nose of the curves being at 650 to 750°C.

4. Healing, which is the recovery of the original corrosion resistance, occurs when the stainless steel is heat treated for a prolonged time at the sensitizing temperature.

5. Increased sensitization can subsequently develop at low temperatures of 300 to 500°C, if chromium carbides are nucleated by a brief exposure at the normal sensitization temperature range (500 to 850°C).

6. The DOS of austenitic stainless steel increases markedly, with increasing carbon content, and to a lesser extent with decreasing chromium content.

7. The presence of either continuous or discontinuous
morphologies of chromium-rich carbides \((\text{M}_{23}\text{C}_6)\) at the grain boundaries, and associated with a chromium depleted region along the grain boundaries.

In practical situations sensitization results from slow cooling from an annealing treatment, slow cooling of a casting or forging, during stress relieving in the temperature range 500 to 850°C, during elevated temperature service, and during welding, which is the most common cause of sensitization.

2.2.2 Mechanisms of Sensitization

Many theories have been proposed to explain the sensitization of austenitic stainless steels: 1) chromium depletion theory, 2) strain theory, 3) noble carbide theory, and 4) solute segregation theory. In describing these theories in the following subsections, the approach of Chung (43) is used.

2.2.2.1 Chromium Depletion Theory

This theory was proposed by Bain and Co-workers (44). According to this theory, detrimental heat treatments results in precipitation of chromium-rich \(\text{M}_{23}\text{C}_6\) carbides along grain boundaries, which is responsible for sensitization, as shown in Figure 3(A) (43). The rapid diffusion of interstitial carbon, and the subsequent precipitation of carbides, depletes the matrix and grain boundary regions surrounding the carbides of chromium. Chromium diffuses much more slowly being substitutional, so chromium must initially be drawn from material adjacent to the carbide, as shown in Figure 3(B) (43). Since chromium is
Figure 3 Schematic depicting: (A) Chromium depleted zone adjacent to grain boundaries, and (B) Chromium depleted concentration profile from a carbide at the grain boundary (43)
responsible for formation of the highly passive film, which makes the stainless steel corrosion resistant, the chromium depleted regions are susceptible to IGC.

This theory predicts that DOS decreases with decreasing carbon content and increasing chromium content, and with the addition of strong carbide formers (like Ti, Nb, etc.). These predictions have been verified (45). At the present time, this theory is universally accepted, since theoretical studies (46-49), direct experimental evidence of chromium depletion at grain boundaries using AEM (9,49,50), and experimental studies (46,51-55) which have correlated the onset of sensitization with the presence of carbides at grain boundaries, have substantiated this theory.

2.2.2.2 Strain Theory

This theory was proposed by Kinzell 35 years ago (56). According to this theory, the lattice is distorted near the chromium carbide precipitate and has a higher strain energy than the rest of the matrix, making these regions of high strain energy susceptible to IGC. The amount of strain energy is related to the orientation between the grains adjacent to the grain boundary, at which the chromium carbide is precipitated.

This theory is disproved by the work of:

1. Younger et al (57) on chromium carbide precipitation, using transmission electron microscopy (TEM), which showed that the precipitates were coherent with one of the adjacent grains. This leads to compositional differences on the two sides of
the boundary, which supports the chromium depletion theory;

2. Povich and-Smith (58) on IGSCC of BWR piping, who showed that stress without a sensitized microstructure did not cause IGSCC. Although strain may influence the chromium carbide precipitation and the diffusivity of chromium, it is not a major reason for IGC of austenitic stainless steels.

2.2.2.3 Noble Carbide Theory

This theory was proposed by Sticker and Vinckier about 25 years ago (59,60). According to this theory, the lattice which is active is galvanically coupled to the noble carbides, causing an electrochemical reaction between the carbides and the lattice along the grain boundaries. This theory is disproved by the work of:

1. Baumel et al (61), France and Greene (62), who showed that IGC occurs even when the stainless steel is in a passive state, in an acid copper sulfate or sulfuric acid solution, where the lattice is at the same potential as the carbide.

2. Aust et al (63), which showed that IGC did not occur even when grain boundary carbides are precipitated, but by heat treating the composition in the alloy is homogenized.

2.2.2.4 Solute Segregation Theory

This theory was proposed by Aust and coworkers about 20 years ago (63-65). According to this theory, the presence of continuous grain boundary paths, of either second phase or solute segregate resulting
from solute-vacancy interactions, is responsible for IGC.

Although experimental evidence (66) supports this theory, in explaining the anomalous IGC of solution-annealed austenitic stainless steel in boiling 5N HNO₃ + 0.46N Cr⁶⁺ solutions; there is criticism (67) that this theory does not place emphasis on the importance of the high oxidizing power of the above environment, which makes the stainless steel transpassive. Even though elements like phosphorus (68) and sulfur segregate to the grain boundary and increase the IGC of sensitized austenitic stainless steel, the mechanism of IGC is still well explained by the chromium depletion theory (69). Segregation of these elements occurs during solution annealing and they affect the nucleation and growth of carbides, while IGC is due to chromium depletion near the growing carbides.

To summarize it seems clear that the chromium depletion theory is widely accepted and valid in most instances, except in IGC of solution-annealed austenitic stainless steel in highly oxidizing corrodents.

2.3 Understanding Sensitization in Terms of Chromium Carbide and Nitride Precipitation

Since sensitization is due to the chromium depletion at the grain boundaries, it is necessary to understand sensitization in terms of chromium carbide and nitride precipitation. For this purpose the treatment of Sedriks (70) and Cihal (71) is considered. The equilibrium relationships, carbon or nitrogen solubility in AISI 304 SS as shown in Figure 4 (70) must first be analyzed. This figure shows that in alloys
Figure 4  Pseudobinary phase diagram for a Fe-18%Cr-8%Ni alloy with varying carbon content (70)
containing between about 0.03 and 0.7 wt.% carbon, the equilibrium structure at room temperature should contain austenite, alpha ferrite, and carbide. But the reaction $\gamma + M_{23}C_6 \rightarrow \gamma + \alpha + M_{23}C_6$ (at line SK) is too sluggish to take place at practical rates of cooling from elevated temperatures. The transformation of austenite to alpha ferrite is ignored in practice. It is seen that the solubility of carbon and nitrogen in austenite decreases drastically with decreasing temperature, but fast cooling can help retain them in solid solution. If this supersaturated austenite containing carbon in excess of 0.03 wt.% is reheated to elevated temperatures within the $\gamma + M_{23}C_6$ field, precipitation of the chromium rich $M_{23}C_6$ will take place at the austenite grain boundaries. In stainless steels with less than 0.03 wt.% carbon alloyed with more than 0.25 wt.% nitrogen, chromium nitrides can also precipitate at the austenite grain boundaries (73). Certain time-temperature combinations will be sufficient to precipitate the carbides and nitrides, but insufficient to rediffuse chromium back into the austenite near the carbides and nitrides. This results in chromium depletion in the austenite around the carbides and nitrides, which causes IGC.

2.4 Thermodynamics and Kinetics of Chromium Carbide and Nitride Precipitation

The chromium depletion theory unambiguously proves that there is a relationship between the IGC and precipitation of carbides and/or nitrides. So the thermodynamics and kinetics of this phenomenon are considered, and experimental AEM verification of these theoretical
models is given in this section. In 2.4.1 thermodynamic calculations are used to: 1) construct TTS diagrams and calculate $X_{Cr}^i$, 2) calculate the maximum temperature for carbides and nitrides to precipitate ($T_s$), the maximum temperature for IGC to occur ($T_M$), and the minimum time for IGC to initiate ($t_{min}$). In 2.4.2 kinetics is used to calculate: 1) the chromium concentration profiles in the vicinity of carbides, 2) the carbon activity at the carbide-austenite interface ($a_C$), $X_{Cr}^i$, and the concentration of carbon remaining in the austenite matrix ($X_C^p$), all as a function of annealing time, and 3) the fraction of carbides, $W(t)$ precipitated out of the total amount of carbides which can be precipitated. In 2.4.3 the effect of the electron probe configuration on the AEM measurements is considered.

2.4.1 Thermodynamics of Carbide and Nitride Precipitation

2.4.1.1 Calculation of TTS diagrams and $X_{Cr}^i$

Thermodynamic modeling of sensitization in austenitic stainless steel has been performed by previous investigators. Stawstrom and Hillert (46) developed a model based on chromium diffusion control to calculate TTS diagrams. They (46) estimated the chromium content at the carbide interface, by considering the changing equilibrium during precipitation of $M_{23}C_6$ in austenite, in the system Fe-Cr-Ni-C.

Tedmon et al (47) used a more general approach to calculate the chromium content at the carbide interface. They (47) considered the reaction:

$$23 \text{Cr} + 6\text{C} = \text{Cr}_{23}\text{C}_6$$

to be in equilibrium at the carbide interface, and applied Wagner's
analysis (74) to calculate the activity coefficient of carbon. The activity coefficient of chromium was obtained in this model by using it as a semi-adjustable parameter, to force a fit to experimental corrosion data.

Fullman (48) has suggested that the activity coefficient of chromium can be calculated by the use of the Kaufman and Nesor (76) formulation of the Fe-Cr-Ni system, and combining them according to an equation suggested by Kohler (79). He (48) incorporated the effects of various alloying elements, however the effect of nitrogen was not considered. Hall and Briant (49) have applied Fullman's technique in their investigation of chromium depletion in the vicinity of carbides in sensitized austenitic stainless steels.

Natesan and Kassner et al (73) have derived an equation to calculate the activity coefficient of carbon in Fe-Cr-Ni-C alloys, but the effect of nitrogen was not considered.

In Chapter 3 on theoretical modeling of sensitization, the model of Stawstrom and Hillert (46) and the approaches of previous investigators (47-49,77), will be used to calculate TTS diagrams and $X_{Cr}^i$, in which the effect of nitrogen is incorporated by using the free energy interaction coefficients of nitrogen on chromium and carbon.

2.4.1.2 Calculation of $T_S$, $T_M$, and $t_{\text{min}}$

The approach of Cihal (78) is used in this section to calculate $T_S$, $T_M$, and $t_{\text{min}}$. The precipitation of carbides and nitrides would occur if the change in free energy ($\Delta G$) is negative. $\Delta G$ at temperature $T$ (in °K) is expressed as:
$\Delta G_T = \Delta H_T - T \Delta S_T$  \[1\]

where $\Delta H_T$ is the change of enthalpy and $\Delta S_T$ is the change of entropy.

The free energy values are tabulated as standard free energies $\Delta G^{\circ}_{298}$. The standard state is the standard form of an element or a compound at $298^\circ K$ and 1 atm. When the temperature dependence of $\Delta H$ and $\Delta S$ is small,

$$\Delta G_T = \Delta G^{\circ}_{298} - T \Delta S^{\circ}_{298}$$  \[2\]

The change of free energy for the formation of carbides and/or nitrides, in a solid solution for a general form

$$nMe + X = mM_{e_{x y}}$$  \[3\]

where $n=m_x$ and $m=1/y$, is given as:

$$\Delta G_T = \Delta G^{\circ}_{T} + RT \ln J$$  \[4\]

where $R$ is the universal gas constant and

$$J = \frac{\overline{a^n_{Me_{x y}}}}{\overline{a^m_{Me_{x y}}}}$$  \[5\]

$a_i$ being activities of reactants and products at a state of non equilibrium. Substituting for $J$ in equation [4]

$$\Delta G_T = \Delta G^{\circ}_{T} = RT \ln \frac{\overline{a^n_{Me_{x y}}}}{\overline{a^m_{Me_{x y}}}} - RT \ln \frac{a^n_{Me_{x y}}}{a^m_{Me_{x y}}}. \frac{\ln K}{-RT_{\ln a^m_{Me_{x y}}}}$$  \[6\]

If the system expressed by reaction [3] attains equilibrium, then $\Delta G_T=0$ and

$$\Delta G^{\circ}_{T} = -RT \ln (J_{eq}) = -RT \ln K = -RT \ln \frac{a^n_{Me_{x y}}}{a^m_{Me_{x y}}}$$  \[7\]

where $K$ is the equilibrium constant of reaction [3] and $a_i$ are the equilibrium activities of the reactants and products. If the carbide and/or nitride which are precipitated are insoluble, $a_{Me_{x y}} = 1$ and

$$\Delta G_T = RT \ln \left(\frac{a^n_{Me_{x y}}}{a^m_{Me_{x y}}} \right)$$  \[8\]

Solving equation [1] gives $T_s$ as:

$$\frac{1}{T_s} = \frac{4.575}{(\ln a^n_{Me_{x y}} + \ln a^m_{x y})}$$  \[9\]
For precipitation of Cr$_{23}$C$_6$ in austenitic stainless steels containing 20 wt.% chromium and 9-40 wt.% nickel (79):

\[
\frac{1}{T_S} = \frac{1}{5500} (2.92 - 0.01 \text{ wt.\% Ni} - \ln \text{ wt.\% C})
\]  

[10]

Analogous to $T_S$, $T_M$ is given by:

\[
\frac{1}{T_M} = \frac{1}{\Delta H} (A - B \text{ wt.\% Ni} - \ln \text{ wt.\% C})
\]  

[11]

where $\Delta H$, $A$ and $B$ are constants. It is seen that the effects of nickel and carbon on $1/T_M$ and $1/T_S$ are analogous, and that a linear relationship exists between them. $T_M < T_S$ as shown in Figures 5a and 5b (71). The dependence of $1/T_M$ and $1/T_S$ on carbon content is linear and the slope of the line does not change for different nickel contents. Therefore the coefficients for wt.\% Ni in equations [10] and [11] are the same. If $T_M$ is reduced by a reduction of $T_S$, the time ($t_{\text{min}}$) needed for IGC to initiate increases, as shown in Figure 5c (71). $t_{\text{min}}$ is given as (80):

\[
\log t_{\text{min}} = \frac{C}{T_M} - D \text{ wt.\% Cr} - E
\]  

[12]

where $C$, $D$ and $E$ are constants. The relationship between $T_S$, $T_M$ and $t_{\text{min}}$ can be used as a means to assess susceptibility to IGC. The difference $1/T_M - 1/T_S$ is called the degree of stabilization and is used to evaluate the stabilizing elements, it is approximately constant with different carbon contents.

A detailed analysis of chromium nitride precipitation is difficult due to lack of data. Also the precipitation of carbo-nitrides is
Figure 5  Dependence of $T_M$ and $T_S$: (A) on the carbon and nickel contents, (B) their mutual relationship; (C) The effect of $T_M$ on $t_{\text{min}}$ (71)
possible, in the presence of carbon and nitrogen in austenite at low sensitizing temperatures (73).

2.4.2 Kinetics of Carbide and Nitride Precipitation

2.4.2.1 Calculation of Chromium Concentration Profiles

Hall and Briant (49) have calculated chromium concentration profiles perpendicular to the grain boundaries in sensitized austenitic stainless steels, using the kinetic model suggested by Zener (81) and expanded by other investigators (82-84). Their (49) approach will be described and used in Chapter 3 on theoretical modeling of sensitization in AISI 304 stainless steels containing nitrogen.

Tedmon et al. (47), Hall and Briant (49), have calculated chromium concentration profiles along the grain boundaries in sensitized austenitic stainless steels. They (47,49) used the approach of Brailsford and Aaron (85) for the growth of precipitates via grain boundary diffusion, which uses Shewmon's method (86). The basic continuity equation to be solved is:

$$\frac{d C_{gb}(r,t)}{d t} = \frac{D_{gb}}{r} \left( \frac{d}{dr} \right) r \left( \frac{d C_{gb}(r,t)}{dr} \right) + F/\delta \quad [13]$$

where $C_{gb}(r,t)$ is the position (r) and time (t) dependent grain boundary chromium concentration, $D_{gb}$ is the grain boundary chromium diffusion coefficient, F is the rate at which solute enters per unit area of the grain boundary, and $\delta$ is the grain boundary width. The solution for equation [13] is given by:

$$C_{gb}(r,t) = C_M - \left( C_M - C_I \right) \left[ f(r)/f(r_I) \right] \quad [14]$$

where $C_M$ is the bulk chromium concentration, $C_I$ is the chromium
concentration at the carbide-austenite interface, \( r_1 \) is the carbide radius, and \( f(r) \) is given by:

\[
f(r) = K_1(\xi R_C)I_0(\xi r) - I_1(\xi R_C)K_0(\xi r)
\]  

[15]

where \( K_0, K_1, I_0 \) and \( I_1 \) are modified Bessel functions, \( R_C \) is the distance beyond which no depletion is detected, and \( \xi \) is given by:

\[
\xi^2 = \frac{D}{D_{gb}} (\pi D t)^{-1/2}
\]  

[16]

where \( D \) is the bulk chromium diffusion coefficient.

Rosolowski (87) has given a more sophisticated treatment, of the problem of precipitate growth via grain boundary diffusion, using the same basic continuity equation as Brailsford and Aaron. But by using numerical integration he (87) did not have to consider only the long time solution. The results of Hall and Briant (49) for AISI 316LN sensitized at 700°C for 100 hours are shown in Figure 6, which shows that the calculations based on both the models of Brailsford and Aaron, and Rosolowski agree with experimental AEM values. Was and Kruger (88), have also calculated the chromium concentration profiles in sensitized Ni-Cr-Fe alloys, as a function of time, temperature and grain size. Their (88) model is described in the following subsection and is used to calculate \( a_C, X_{Cr}^i \) and \( X_C^\gamma \).

2.4.2.2 Calculation of \( a_C, X_{Cr}^i, \) and \( X_C^\gamma \), all as a Function of Annealing Time.

Was and Kruger (88) used the same basic continuity equation as Hall and Briant (49), which is given below:
Figure 6  Calculated chromium concentration profiles (dashed lines) along a grain boundary, away from an isolated $M_{23}C_6$ carbide in 316 LN, sensitized at 700°C for 100h. Curves B-A1 and B-A2 were calculated using the model of Brailsford and Aaron with $D_{gb} = 1.8 \times 10^{-9}$ cm$^2$/sec and $1.8 \times 10^{-11}$ cm$^2$/sec respectively. Curve R was calculated using the model of Rosolowski. Superimposed on the calculated profiles are the experimental AEM data from 5 different grain boundaries. (49)
where \( C(r,t) \) is the position \((r)\) and time \((t)\) dependent chromium concentration. But in their (88) model equation \([17]\) is discretized and solved numerically, and is a modification of the diffusion-controlled reaction model of Stawstrom and Hillert (46). \( a_C^x \), \( x_{Cr}^1 \), and \( x_C^Y \), as a function of annealing time for 18-8 steel with 0-10 wt.% carbon, given by Stawstrom and Hillert (46), are shown in Figure 7. It illustrates that \( a_C \) decreases, \( x_{Cr}^1 \) increases, and \( x_C^Y \) decreases, with annealing time, which is expressed as a dimensionless parameter \((r)\)

\[
 r = \frac{D t}{h^2} \tag{18}
\]

where \( h \) is the grain size.

2.4.2.3 Calculation of \( W(t) \)

The approach of Cihal (89) is used for this calculation. While considering precipitation of carbides or nitrides at the grain boundaries, the diffusion of chromium and carbon (or nitrogen) to the interface between the carbide (or nitride) and austenite must be taken into account. The one with the lowest coefficient of diffusion will exhibit the highest change of concentration in the vicinity of the precipitate.

The precipitation of carbides or nitrides can be expressed for very short time steps, in which a sequence of constant conditions is assumed:

\[
x = a t \tag{19}
\]

where \( x \) is the growth rate, \( a \) is a constant, and \( t \) is the time.

For longer times the following relationship is satisfied:
Figure 7  $a_C$, $x_{Cr}^{i}$ and $x_C^i$, all as a function of annealing time (46)
\[ x = a \cdot t^n \]  
where \( n \) is a constant.

Equation [20] is based on the general relationship:
\[ \frac{x}{x_0} = 1 - \exp(-a \cdot t^n), \text{ from which} \]
\[ W(t) = 1 - \exp(-a \cdot t^n) \]  

The amount of \( \text{M}_{23}\text{C}_6 \) carbide precipitated at 600 - 700°C was investigated by Cihal (89), and the activation energy of precipitation was found to be around 300 kJ.mole\(^{-1}\), which corresponds to the activation energy of diffusion of chromium in austenite.

2.4.3 **Effect of Electron Probe Configuration on AEM Measurements**

The effect of electron probe configuration on AEM measurements can improve the agreement between measured and calculated chromium concentration profiles. It has been estimated analytically by previous investigators (90-94). In this approach the electron beam intensity distribution through the thickness of the foil and the concentration profile across the grain boundary are considered to be Gaussian functions. Application of the principles that led to the Cliff-Lorimer relation for thin foils relates the X-ray intensity to the concentration. If the electron beam broadening is considered to be given by the single scattering model, we can calculate the concentration. Hall and Briant (49) improved the agreement between the calculated and experimentally determined chromium concentration profiles across the grain boundaries of sensitized austenitic stainless steels, by considering the above model. The detailed description of this model is given in Chapter 3 on theoretical modeling of sensitization and this
model will be applied to sensitized AISI 304 SS containing nitrogen.

2.5 Factors Affecting Sensitization

Now that the thermodynamics and kinetics of carbide and nitride precipitation have been understood, the various factors affecting sensitization can be studied. To understand the effect of various factors on sensitization the treatment of Cihal (95) and Chung (96) is used. Sensitization depends on a large number of factors which control carbide precipitation and chromium depletion. These factors can be grouped as follows:

1) Effect of Chemical Composition
2) Effect of Sensitizing Temperature and Time
3) Effect of Microstructure and grain size
4) Effect of Cold Work and Pre-heat-treatment
5) Effect of Stress
6) Effect of Potential
7) Effect of Radiation

2.5.1 Effect of Chemical Composition

The effect of chemical composition can be understood by studying the influence of carbon, nitrogen, alloying elements, minor elements, and stabilizing elements. In Section 2.4 it was shown that $t_{\min}$ is a function of the diffusion coefficient ($D$), the amount of carbon and chromium, and the grain size. For a steel of given composition, after solution annealing, the amount of carbon, chromium and grain size are constant. Therefore, the dependence of $D$ on temperature is:
\[ D = D_0 \exp(-Q/RT) \]  \[22\]

which can be expressed by a linear relationship between \( \log t_{\text{min}} \) and \( 1/T \), the slope of which gives the activation energy (\( Q \)) of the process, controlling the rate of development of sensitization.

2.5.1.1 Effect of Carbon

If the TTS curves (Figure 8) for steels containing various carbon contents are analyzed in the manner described above \(95\); for the steels with greater than 0.03 wt.% carbon, in the low temperature range the activation energy is high and corresponds to diffusion of chromium. In the high temperature range the activation energy is low and corresponds to grain boundary diffusion of carbon or chromium. For the steels with lower than 0.03 wt.% carbon, the activation energy is low even at low temperatures. So for the higher carbon steels, chromium diffusion becomes the controlling process below a certain temperature leading to sensitization.

To prevent sensitization the carbon content must be lowered. The maximum carbon content for which the steel does not become sensitized, depends on the presence of nitrogen, other alloying elements like chromium, nickel, molybdenum, silicon, manganese, as well as on minor elements and stabilizing elements.

2.5.1.2 Effect of Nitrogen

The effect of nitrogen on sensitization is yet to be fully understood. Early studies by Binder et.al. \(51\) showed that a maximum in sensitization occurred at 0.04 wt.% nitrogen (Figure 9), and Grutzer
Figure 8  TTS diagrams and 1/T vs log $t_{\text{min}}$ for stainless steels containing various carbon levels (95)
Figure 9 Influence of nitrogen content on the (A) depth of intergranular penetration of 18 wt.% chromium, 0.02-0.03 wt.% carbon stainless steels in the Strauss test (51), (B) TTS diagrams for a 18%Cr-11%Ni austenitic stainless steel (73)
Sheridan and Kieffer (97) showed that the detrimental effect increases with increasing nitrogen additions (Figure 9). Later studies (98) have showed that an increase in nitrogen content to around 0.15-0.20 wt.% has no significant influence on sensitization. However, recent studies have shown that nitrogen additions retard sensitization, though the mechanisms involved have not yet been fully understood (7-9,69).

Eckenrod and Kovach (7) showed that TTS diagrams constructed using metallographic techniques for AISI 304 SS containing 0.04 to 0.25 wt.% nitrogen indicate that nitrogen up to 0.16 wt.% retards sensitization (Figure 10) and Huey test ratings (Figure 11) were consistent with those of the TTS curves.

Briante et al. (8) showed that, nitrogen additions to high purity AISI 304 SS delays sensitization, and the amount of improvement depends on both the carbon content and the sensitization temperature. They (8) showed evidence that nitrogen acts to retard the nucleation and/or growth of carbides at grain boundaries, and hence increases the time necessary for sensitization. Mulford et al. (9) showed that nitrogen additions to commercial purity AISI 304 SS had a beneficial effect on sensitization, but the improvement was less than in high purity alloys. Figure 12 shows a constant improvement in sensitization behavior with increasing nitrogen additions to AISI 304LN in the temperature range 650 to 800°C (9). Briante et al. (8) suggested that the observed improvements could occur by a number of mechanisms:

1. Retardation of the nucleation and/or growth of the carbides,
2. Changes in the activity of chromium in equilibrium with the
Figure 10 TTS diagrams for AISI 304 SS containing nitrogen, which indicates that nitrogen upto 0.16 wt.% retards sensitization (7)
Figure 11 Huey test results on sensitized AISI 304 SS containing nitrogen (7)
Figure 12 Improvement in sensitization behavior with increasing nitrogen content for AISI 304 LN alloys. 304 LN-A, 304 LN-B, 304 LN-C have 0.13, 0.11 and 0.08 wt.% nitrogen respectively (9).
carbide,
3. Changes in the ease of passivation of the alloy so that more chromium depletion is required to cause failure, and
4. Prevention of martensite formation upon quenching,

stated that no data were available for the effects of nitrogen on the activities of carbon and chromium at the sensitization temperatures. The effect of nitrogen on sensitization of AISI 304 SS is studied in the present investigation and the theoretical modeling, experimental procedures, results and analysis, discussion, summary and conclusions of this investigation will be described in detail in the following chapters.

2.5.1.3 Effect of Alloying Elements

It was stated in subsection 2.5.1.1 that various alloying elements like chromium, nickel, molybdenum, silicon, and manganese affect the maximum carbon content for which the steel does not become sensitized. In order to include the influence of chromium and nickel, the concept of effective carbon content is introduced, which is generally expressed by the relationship:

\[ C' = \%C + k_1(\%Ni-k_2) \] [23]

which shows that while chromium has a favorable effect, nickel does not (95). In the above equation \( k_1 \) and \( k_2 \) are constants. The work of Perkins and Carlson (99) has shown that chromium decreases the diffusivity of carbon and precipitation of carbides. Baokov et.al. (100) has shown that nickel decreases carbon solubility in austenite causing increased sensitization.
The presence of molybdenum increases the effective chromium content \( \text{Cr}' \), which can be expressed as:

\[
\text{Cr}' = \%\text{Cr} + b(\%\text{Mo})
\]  

[24]

where \( b \) is a constant (95). Seferian (101) has shown that molybdenum retards the precipitation of the carbides. Briant et. al. (8) have shown that molybdenum increases the ease with which the steel passivates, and the combination of molybdenum plus nitrogen retards the nucleation and/or growth of carbides, while molybdenum alone does not have this effect.

At present there is lack of sufficient data on the quantitative influence of silicon and manganese on the above relationships, but qualitatively both are detrimental to sensitization (102-105). However, manganese was beneficial at low sensitizing temperatures in the presence of nitrogen (8). Based on the effect of various alloying elements, the equation for drawing the dividing line between regions where sensitization does not occur and does occur has the general form:

\[
\text{Cr}' = K + \alpha.C'
\]  

[25]

where \( \alpha = 100 \) and \( K = 16 \) (95).

2.5.1.4 Effect of Minor Elements

The minor elements like phosphorus, sulfur, boron, etc., segregate to the grain boundaries and affect the nucleation and early growth of carbides by changing the vacancy concentration at the grain boundaries (69). Phosphorous accelerates IGC in the Huey tests (66-69,106) and promotes the nucleation of \( \text{M}_{23}\text{C}_6 \) precipitates on the (111) matrix planes (107). Sulfur combines with chromium to form chromium sulfides, both in
the matrix and along grain boundaries, leading to pitting across the entire sample surface in the nitric acid and oxalic acid tests (69). Boron suppresses precipitation of $M_{23}C_6$ at the grain boundaries (108) or increases precipitation of borides (109, 110). There is as yet no unambiguous explanation of the effect of boron on susceptibility to IGC (111-113). The effect of minor elements on IGC depends on the interactions between them and other alloying elements (68).

2.5.1.5 **Effect of Stabilizing Elements**

The stabilizing elements like titanium and niobium have a greater affinity for carbon than chromium and form highly stable carbides ($TiC$ and $NbC$). In this manner the formation of a continuous network of $Cr_{23}C_6$ at the grain boundaries is prevented. The addition of stabilizing elements in a quantity close to the theoretical level relative to the carbon content is quite inadequate for stabilizing the steels because they combine with nitrogen and other elements.

The total titanium content in steel can be expressed as (95):

$$Ti = Ti_{TiC} + Ti_{TiN} + Ti_{Ti_2S} + Ti_y$$  \[26\]

where $Ti$ is the total titanium content in the steel, $Ti_{TiC}$, $Ti_{TiN}$, and $Ti_{Ti_2S}$ is titanium combined with carbon, nitrogen and sulfur respectively, and $Ti_y$ is free titanium dissolved in austenite. Exact data on the content of titanium bonded to $Ti_2S$ is not available, and it is generally assumed that roughly half of the sulfur present is bonded to $Ti_2S$ (114). Expressing the titanium content bonded to nitrogen using the following equation (115):

$$Ti_{TiN} = 3.43(N - 0.001)$$  \[27\]
where \( %N \) is the percentage of nitrogen in the steel, the following relationship for titanium combined with carbon can be written (95):

\[
\text{Ti}_{\text{TiC}} = \text{Ti} - 1.5\% \text{S} - 3.43(\% \text{N} - 0.001) - \text{Ti}_y
\]

[28]

and for combined carbon content (95)

\[
\text{C}_{\text{TiC}} = \frac{\text{Ti}_{\text{TiC}}}{4} = \frac{\text{Ti} - 1.5\% \text{S} - 3.43(\% \text{N} - 0.001) - \text{Ti}_y}{4}
\]

[29]

Since there is at present less data on the dissociation of TiC, \( \text{C}_{\text{TiC}} \) is replaced on the basis of statistical analysis by the 'efficiency coefficient' (\( f \)), so:

\[
\text{C}_{\text{TiC}} = f \frac{\text{Ti} - 1.5\% \text{S} - 3.43(\% \text{N} - 0.001)}{4}
\]

[30]

To determine susceptibility to IGC, it is advantageous to use the relationship derived for unstabilized steels, in such a form that the effective free carbon content is expressed by (95):

\[
\text{C}' = \% \text{C} + k_1(\% \text{Ni} - k_2) - f \frac{\text{Ti} - 1.5\% \text{S} - 3.43(\% \text{N} - 0.001)}{4}
\]

[31]

As a rule of thumb the amounts of titanium and niobium required for stabilization are 6 and 10 times the carbon content, respectively (101,116,117).

2.5.2 Effect of Sensitizing Temperature and Time

Binder et.al. (51) were among the first to use TTS diagrams to demonstrate the effects of sensitizing temperature and time.

2.5.2.1 Effect of Sensitizing Temperature

The effect of sensitization temperature can be understood in terms
of thermodynamic control at high temperatures and kinetic control at low
temperatures. Stawstrom and Hillert (46), Tedmon et al. (47), Was and
Kruger (88), have all shown that $X_{Cr}^i$ increases with increasing
temperature, and at temperatures above 850°C $X_{Cr}^i$ increases to above
11-12 wt.%, making the steel immune to sensitization even though
carbides are present. At the low temperatures sensitization is limited
by diffusion of chromium in austenite, since the diffusion coefficient
of chromium drops over three orders of magnitude from 700 to 500°C.
Although nucleation of carbides occurs, their growth would not take
place below 500°C because of the slow diffusion of chromium (116).

2.5.2.2 Effect of Sensitizing Time

Initially sensitization increases with sensitizing time because of
the depletion of chromium around the growing carbides, but after long
times sensitization decreases because chromium concentration near the
carbides will level off (114). Figure 13 shows the variations of
chromium content in the vicinity of carbides with increasing
sensitization time. Until time $r_0$ when precipitation of carbides begins,
the chromium is evenly distributed throughout the solid solution. After
time $r_1$ as carbides precipitate, depletion takes place in the close
vicinity of these carbides. As time increases to $r_2$ and $r_3$, the depleted
area gradually expands and the level of chromium between the carbides
drops along the grain boundaries, due to the faster diffusion until
overlapping depletion regions are formed along the grain boundaries.
After time $r_4$ and $r_5$, carbon needed for precipitation of carbides
becomes sparse and diffusion of chromium will continue so that chromium
Figure 13 Variations of chromium content in the vicinity of carbides with increasing sensitization time, $t_0$-$t_6$ in AISI 304 SS. (A) Schematic variations of chromium content near two carbide particles; (B) lines indicating identical contents of chromium (section perpendicular to the boundary) (114)
concentration near the carbides will level off. Finally during the closing stage approaching equilibrium, $r_6$, the concentration of chromium within the whole grain will be lower because of chromium used up for precipitation of carbides.

2.5.2.3 Combined Effect of Sensitizing Temperature and Time

DOS is dependent on thermodynamics and kinetics which have opposing effects. For example, $X_{Cr}^i$ decreases (DOS increases) at low sensitizing temperature and time, while nucleation and growth of carbides increases (DOS increases) at high sensitizing temperature and time. So maximum DOS occurs at a certain combination of sensitizing temperature and time.

2.5.3 Effect of Microstructure and Grain size

2.5.3.1 Effect of Microstructure

Chromium carbides ($Cr_{23}C_6$) begin to form first at the ferrite-austenite interface, they then appear at austenite grain boundaries, and later on at incoherent boundaries between twins and finally at the coherent boundaries of twins (89,120). Carbide precipitation at the ferrite-austenite interface is faster than at austenite grain boundaries (60,100), because the diffusivity of chromium in ferrite is about 3 orders of magnitude faster than in austenite (121,122). Distribution of carbides at the grain boundaries also affects sensitization. Since the chromium concentration gradient along the grain boundary between carbides is controlled by (47,49): 1) spacing between carbides, 2) grain boundary diffusivity of chromium, and 3) $X_{Cr}^i$; under certain heat treatments the grain boundary will not be
continuously depleted of chromium.

Precipitation of chromium nitrides (Cr$_2$N) at grain boundaries and lamellar nitrides similar to pearlite, in austenitic stainless steels with high nitrogen/carbon ratio, leads to IGC as shown in Figure 14 (89), which shows C curves for 1) precipitation of chromium nitrides at grain boundaries, 2) lamellar nitrides similar to pearlite, 3) chromium carbides at grain boundaries of nitrogen-free steel, and 4) onset of IGC (89). Titanium carbide present in stabilized steels can be attacked in strong oxidizing acids and if precipitated at grain boundaries they could lead to IGC. For this reason stabilization with niobium is preferred (123). Formation of intermetallic compounds especially sigma-phase is deleterious in strong oxidizing acids, because phases rich in chromium and molybdenum, dissolve easily in strong oxidizing acids than phases low in these elements and richer in nickel (124). The effect of chi-phase on the corrosion behavior of steels modified with molybdenum is not well understood (89). If transformation of austenite into martensite occurs upon quenching then susceptibility to IGC increases (120).

2.5.3.2 Effect of Grain Size

The effect of grain size is difficult to study, because thermal and mechanical treatments given to vary grain size can cause changes in grain boundary chemistry and structure. Early work by Newell (125) showed that increasing grain size increased susceptibility to sensitization. This was explained by Cihal (126) in terms of less chance for a continuous network of carbides to form at the numerous grain
Figure 14 C curves for: (A) Precipitation of chromium nitrides at grain boundaries, (B) Lamellar nitrides similar to pearlite, (C) Chromium carbides at grain boundaries of nitrogen free steels, and (D) onset of IGC (89)
boundaries in a small grained material. But more recent work by Levin and Kaloshina (127), who minimized the thermal effects by giving the same final anneal, found no effect of grain size on IGC in acidified copper sulfate. This was explained by Streicher (128,129) in terms of the different experimental methods and test solutions which influence the effect of grain size, for example the effect of grain size is overshadowed by the influence of the accumulated corrosion products, which speed up the attack in boiling nitric acid. In spite of such conflicting evidence, it has generally been accepted that increasing grain size increases susceptibility to sensitization. Influence of grain size on IGC, taking the chemical composition into account, can be expressed as (95):

$$f(N) \cdot (Cr' - Cr_o) + C_o > C'$$

where \( f(N) \) is a function proportional to grain boundary surface area per unit volume, \( Cr' \) and \( C' \) are the effective chromium and carbon contents defined by equations [25] and [31] respectively, \( Cr_o \) and \( C_o \) are the grain size dependent constants indicating the chromium and carbon contents for which there is no sensitization respectively.

2.5.4 Effect of Cold Work and Pre-Heat-Treatment

2.5.4.1 Effect of Cold Work

It is known that austenitic stainless steels are often partially transformed to martensite during cold work, which led Henthorne (113) to point out that martensite would be preferentially attacked. But Cihal (95) has showed that martensite formed by cold working is not the main cause of sensitization, and its presence does not constitute the basis
of the increase in sensitization especially at high levels of cold work. The reason for this is the same influence of cold work that is seen on IGC of: 1) steels sensitized at 625°C for 3 hours and deformed either at room temperature or at a higher temperature, at which the martensite transformation is impossible, and 2) steels in which the austenite-to-martensite deformation is prevented by stabilizing the austenite with large nickel additions. The influence of cold work on sensitization depends on: 1) whether the cold work is given before or after sensitization, 2) the amount of cold work, and 3) the sensitizing and cold working temperatures.

High levels of cold work of about 50% before sensitization decrease susceptibility to sensitization at sensitizing temperatures of 600 to 850°C, because of carbide nucleation sites within the deformed grains; for example, precipitation on dislocations reduces the amount of carbide precipitated at grain boundaries. At high levels of cold work, chromium is more easily restored by diffusion to areas previously depleted of it (44,47,95,130,131). But at high sensitizing temperatures above 850°C recrystallization gradually eliminates the influence of the prior cold working (95). Low levels of cold work of about 5% before sensitization increase susceptibility to sensitization at a sensitizing temperature of 650°C, because the influence of working is limited to grain boundaries (95). At the grain boundaries dislocation pile up occurs, enhancing the diffusion of chromium to the grain boundary, and promoting sensitization (132). DOS increases with post-sensitization cold work of up to 10% and subsequently falls to a value lower than that corresponding to the original state (95).
2.5.4.2 Effect of Pre-Heat-Treatment

Vermilyea et al. (133) showed that, instead of water quenching after solution annealing, furnace cooling or isothermal heat treatments in the temperature range 800-1050°C, retard sensitization upon subsequent heating at lower temperatures. This is because the problem of excess quenched in vacancies is eliminated, leading to slower development of the grain boundary carbides. Cooling to subzero temperatures after sensitization increases susceptibility to IGC and cooling before sensitization produces an opposite effect. This is because in the latter case carbide precipitation is spread over a greater area (i.e. martensite is formed) instead of just at the grain boundaries (95).

2.5.5 Effect of Stress

It has been reported that sensitizing the steel is conducive to a change from transgranular to intergranular in the character of SCC in chloride-containing media; so elimination of sensitivity to IGC can be a means of decreasing susceptibility to SCC (95). The present investigation will be correlating sensitization to SCC susceptibility.

2.5.6 Effect of Potential

The approach of Cihal (95) is used to understand the effect of potential on IGC. The susceptibility to IGC is dependent on the nature of the grain boundaries depleted of chromium, and consequently on the passivating potential, critical passivating current density and current
density in the passive condition. Chromium content is essential for these parameters, nickel is unimportant up to 30 wt.%; temperature is important with current densities increasing with increasing temperature. Figure 15 shows zones of susceptibility to IGC as a function of potential and annealing time (135). Up to a potential of 0.2 $V_H$, both the grain and the boundary are active and general corrosion occurs (134). Up to a potential of 0.5 $V_H$, which corresponds to the passivating potential for iron, the grain passivates and the depleted sensitive grain boundary is active and corrodes considerably. Above this potential, the boundary depleted of chromium passivates, and IGC is based only on various rates of corrosion of the two regions in the passive condition (135). Higher rates of corrosion of the boundary and/or grains at potentials above 1.0 $V_H$ are connected with: 1) a lower-quality and fast dissolving passive layer, and 2) the current density in the passive state. The corrosion rate increases with temperature and potential near entry into the transpassive region. At potentials above the transpassive potential of the grain (1.2 $V_H$) the nature of corrosion differs from IGC in the passive state; crater-like attack occurs at the boundaries which are in a passive state, and whole grains fall out (136,137).

2.5.7 Effect of Radiation

The approach of Cihal (95) is used to understand the effect of radiation on IGC. Radioactive radiation has a severe effect on the redox properties of the environments and thus initiates IGC. Radiation makes water release products of irradiation as shown below:
Figure 15 Zones of susceptibility to IGC as a function of potential and annealing time (135)
The formation of oxidants in irradiated solutions shift the stainless steel potential from the passive condition toward positive values, increasing the corrosion rate of the steel. The radiation effect is observed in nuclear reactors, where an overpressure of hydrogen, which is released, is a factor retaining the reducing conditions and the low corrosion rate. Fujita et al. (138) investigated the effect of gamma ray irradiation on SCC of sensitized AISI 304 SS in high temperature water, and found that IGSCC was accelerated by radiation exposure when high dissolved oxygen was present in the water. Cowan and Tedmon (139) found that irradiated stainless steel is susceptible to IGC because gamma radiation causes oxidation of Cr$^{3+}$ (which is produced during general corrosion) into Cr$^{6+}$. In the case of a nuclear reactor, the radiation is severe and the corrosion potential of the stainless steel will move to noble values even in deaerated solutions. Moreover, the neutrons increase the number of defects in the oxide layer on the steel and increase the corrosion rate.

2.6 EPR Test to Detect Sensitization

The description given here is given in detail by Majidi and Streicher (140,141). The problem of IGSCC failures of sensitized weldments in AISI 304 SS piping in BWRs created a need for a rapid, quantitative, nondestructive and a portable method to detect sensitization. ASTM Recommended Practice A262 describes five different standardized methods for detecting sensitization (142), none of which are both quantitative and nondestructive. Even though the oxalic acid
etch test (Practice A in A262) is rapid and nondestructive, it is not quantitative. Although the other four tests: nitric acid test, acid ferric sulfate test, acid copper sulfate test, and nitric-hydrofluoric acid test, are quantitative they require testing of a small sample in hot, concentrated acids for periods varying from 4 to 240 hours. To meet all the requirements stated above Clarke et al. (143-145), selected the single loop EPR technique proposed by Cihal et al. (146) and Prazak (147), and developed by Novak (148) and others (149-151).

2.6.1 **Single Loop EPR Test**

The surface to be tested is immersed in a deaerated solution of 0.5M H₂SO₄ + 0.01M KSCN at 30°C. The specimen, two counter electrodes and a calomel reference electrode are connected to the potentiostat. After the corrosion potential is determined, the specimen is passivated by holding the potential (E) in the passive range. Then the potential is reversed at a constant rate back to the corrosion potential, during this reversal the current (I) flow is measured. The area under the E vs log I curve, can be used to calculate the total quantity of electric charge (Q) passing through the surface exposed to the solution, as shown in Figure 16(A) (140). While the potential is reversed (reactivation process), the film over the chromium-depleted areas is more readily dissolved than that over undepleted areas of the surface. Hence a sensitized steel generates a larger corrosion current and a larger shaded area in Figure 2-16A, than a solution annealed stainless steel undepleted of chromium over the entire surface. Q must be adjusted for the grain size of the test specimen as suggested by Clarke et al. (149):
Figure 16 Schematic diagram of the EPR test: (A) Single loop version (B) Double loop version (140, 141)
\[ P_a = \frac{Q}{\text{GBA}} \]  

where \( P_a \) is a parameter adjusted for grain size and has units of coulombs/cm\(^2\). \( \text{GBA} \) is the total grain boundary area given as:

\[ \text{GBA} = A_s [5.09544 \times 10^{-3} \exp(0.34696X)] \]

where \( A_s \) = the specimen area and \( X \) = the ASTM grain size number usually determined at a magnification of 100. Since assumptions regarding the width of the attack in sensitized material and the uniformity of the attack over the entire grain boundary area are made in the derivation of the above equation, values of \( P_a \) do not correspond to a literal, well defined corrosion process, but are rather useful indicators of the DOS.

2.6.2 Double Loop EPR Test

In the field it takes a long time to prepare a 1 \( \mu \)m polish on the pipes for the single loop EPR test. This led Akashi et al. (152) to develop the double loop EPR test. This test is described in detail in Chapter 4 on Materials and Experimental Procedures. Briefly, as shown in Figure 16(B) (141), the reactivation scan from a potential in the passive range is preceded by an anodic polarization scan from the corrosion potential into the passive range. The ratio of the maximum currents generated in the two loops \( (I_p:I_a) \) gives a measure of DOS. The advantages of this test are that it is not necessary to polish the surface to a 1 \( \mu \)m finish and it is not necessary to normalize the ratio of maximum currents with a grain size factor.
2.7  **Prevention of Sensitization**

Many methods to prevent sensitization have been developed (95). The most important of these are reducing the carbon content; stabilizing the steel with titanium, niobium, or tantalum; heat treatment; or increasing the ferrite content in the steel structure.

Since sensitization is due to chromium depletion as a result of chromium carbide precipitation, the best way to prevent it is to reduce the carbon content so that precipitation of chromium carbides is avoided. But lowering the carbon content degrades the mechanical properties of the steel, so nitrogen can be added to retain the mechanical properties. The effect of nitrogen on sensitization must be understood, which is one of the aims of the present investigation.

The most widely used means of preventing sensitization is to alloy stainless steels with elements having a greater affinity for carbon than chromium. For example with titanium, niobium, tantalum, zirconium, tungsten and vanadium; with the most stable carbides formed by titanium, niobium and tantalum. This prevents precipitation of chromium carbides and sensitization.

Solution annealing followed by rapid cooling can prevent sensitization by dissolution of chromium carbides.

Two-phase stainless steels consisting of austenite and ferrite, with a reduced nickel content and an increased chromium content, prevent sensitization. The reason for this is that chromium reduces the activity of carbon, whereas nickel increases the activity of carbon; the effect of high chromium and low nickel is to reduce the activity of carbon. Therefore the chromium content in equilibrium with $M_23\text{C}_6$ is
increased. The beneficial effect of ferrite is also due to chromium carbides precipitating preferentially at the austenite/ferrite interface. Therefore, the amount of carbide precipitating and the continuity of chromium depletion at the austenite/austenite interface decreases.

2.8 **Relationship Between Sensitization and IGSCC**

The relationship between sensitization and IGSCC is described in detail by Cihal (95). IGSCC like sensitization is connected with precipitation of chromium carbides. The role of stress in IGSCC may often be only to open up a way for the local corrosion attack to develop at the grain boundary. This facilitates the penetration of the aggressive medium into the boundaries, and promotes the removal of the corrosion products from the crevices. The factors involved in reducing susceptibility to sensitization are also useful in improving resistance to SCC. Ford et.al. (153) state that there is a sound theoretical foundation for asserting that lowering the DOS of the stainless steel will lower the risk of IGSCC in the sensitized AISI 304 SS/water system at 288°C. They (153) further state that preliminary theoretical studies confirm that this result can be offset by the presence of anionic impurities in the water. Since the SCC tests in the present investigation were carried out in high temperature aqueous sulfate and chloride solutions, the correlation between sensitization and IGSCC in this environment will be presented in the subsequent chapters, and compared with Ford's prediction regarding the presence of anionic impurities in the water.
Now that the phenomenon of sensitization has been described in
great detail the phenomenon of SCC will be considered in the subsequent
sections.

2.9 **SCC of Austenitic Stainless Steels**

SCC refers to cracking caused by the simultaneous presence of a
tensile stress and a specific corrosive environment (1). SCC involves
initiation and propagation of a high aspect ratio crack either
intergranularly or transgranularly, at rates of $10^{-7}$ mm s$^{-1}$ to $10^{-1}$ mm
s$^{-1}$. Although austenitic stainless steels have excellent resistance to
general corrosion in a variety of aggressive environments, they suffer
from severe SCC.

2.9.1 **Characteristics of SCC**

The following observations are typical characteristics of SCC of
austenitic stainless steels (154):

1) tensile stress is a necessary condition, which may be in the
form of residual stress, external applied service stress or
wedging forces produced by corrosion products in cracks;

2) generally the alloy is almost inert to the environment which
causes cracking, for example the typical general corrosion rate
of austenitic stainless steels is about 80 to 130 μm (3 to 5
mils) per 40 years of reactor service, but they undergo severe
SCC in the same environment;

3) SCC occurs in only certain combinations of alloys and
environments, for austenitic stainless steels the environments
are Cl\(^-\), OH\(^-\), and H\(_2\)O(O\(_2\));

4) the necessary corroden species need not be present in large quantities in the bulk environment, for example concentration of Cl\(^-\) as low as a few parts per million (ppm) in the bulk aqueous solution causes SCC of austenitic stainless steels (however the local concentration of Cl\(^-\) in the crack tip will be very high compared to that in the bulk);

5) stress corrosion cracks are brittle in morphology, and propagate along grain boundaries (intergranularly) or across grains (transgranularly);

6) there is a threshold stress intensity, and a critical crack tip strain rate below which SCC does not occur;

7) most pure metals do not suffer SCC, but there are some exceptions;

8) only a small fraction of the strength is needed to cause SCC;

9) temperatures substantially above room temperature may be required to activate some process essential to SCC;

10) stress corrosion life is divided into the initiation and propagation periods, however initiation process occurs relatively rapidly (say, one week) in comparison to design lives of 40 years, and propagation process dominates the component life (155).

2.9.2 Mechanisms of SCC

According to Ford (156,157), the advances in mechanistic understanding of SCC have occurred in three distinct phases. The first
was an identification phase in the 1940s and 1950s, in which the problem was identified and categorized in terms of specific alloy/aggressive anion couples, for example, austenitic stainless steel in $\text{Cl}^-$, $\text{OH}^-$, and $\text{H}_2\text{O}(\text{O}_2)$. The second was a mechanistic phase in the 1960s and early 1970s, 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 rates observed. In the present third phase mechanistic knowledge is being applied to practical needs, for example, in improving predictive capabilities through knowledge of rate-determining steps in the cracking mechanism, in giving guidelines to the development of material compositions or environmental control to improve cracking resistance, in developing testing techniques which are relevant to practice and could incorporate their results into a design criterion, and in identifying the actual environmental and material conditions present in components which could lead to SCC.

According to Ford (155, 156) the advance in mechanistic understanding of environmentally controlled phenomena has been documented in the proceedings of a series of conferences (158-168). Table 2-1 shows the classification of Ford (155, 156), and is used to describe briefly the various mechanisms proposed to explain SCC. The various mechanisms proposed to explain the SCC phenomenon have been classified by various authors as follows:

1) Dean (169) has classified them into 2 broad categories, electrochemical theories and quasi-mechanical theories;
2) Sedricks (170) has classified them into 3 broad categories,
dissolution models, mechanical models, and mixed mechanisms;

3) Ford (155,156) has classified them into three broad categories as proposed by Parkins (171), pre-existing active path mechanisms, strain-assisted active path mechanisms and adsorption-related mechanisms.
Table 1
Classification of Various Mechanisms to Explain SCC Phenomenon (155,156)

**Pre-existing Active Path Mechanisms**
These relate the cracking susceptibility to the chemical activity of the grain boundary due to either its inherent disordered structure, presence of chemically active grain boundary impurities and precipitates, or the solute denuded zone adjacent to the precipitate. These attribute little importance to the stress (172).

**Adsorption Related Mechanisms**
These rely on the decrease in mechanical strength at the crack tip due to adsorption of specific species from the environment, followed by possible absorption into the underlaying matrix. These rely heavily on the stress component (161-164,173).

**Surface Energy Reduction Theory**
The surface chemisorption of species from the environment reduces the surface energy and the local fracture stress of the metal lattice, causing atom-atom rupture on the crack tip surface (174).
Decohesion Theory

The absorption and transport of hydrogen or temper-embrittling elements to specific metallurgical sites like inclusions or high triaxial stress regions, causes atom-atom rupture below the crack tip surface by a reduction in atom-atom bond strength (175). Other criteria for decohesion are; formation of pressurized pockets of hydrogen gas due to hydrogen atom recombination (176), brittle phases (e.g. hydrides (177), hydrogen/strain-induced martensite (178), etc), or modification of the flow stress in front of the crack tip by the hydrogen concentration (179).

Non-equilibrium Hydrogen Transport Theory

The diffusion of hydrogen is accelerated by dislocation transport, leading to hydrogen supersaturation at various sites, causing local fracture due to brittle phase formation, restricted plasticity, etc. (180).

Strain-Assisted Active Path Mechanisms

These relate crack propagation to dissolution at the crack tip and the stress/strain condition in that region. These place equal importance on the chemical and mechanical aspects of crack propagation.
Tensile Ligament theory
The corrodent reduces the load bearing area of the tensile ligaments across the crack tip opening by dissolution, thereby lowering the stress intensity required for subcritical crack advance (181).

Mechanochemical Theory
The dissolution at the film-free crack tip is enhanced by the strain concentration because of an increase in active site density, or a decrease in the activation enthalpy for dissolution (182).

Film Rupture Theory
The passive film at the crack tip is ruptured by localized plastic deformation, causing a rapid dissolution of the exposed bare crack tip while the non-deforming crack walls remain protected by the film (183).

Slip Dissolution Theory
The passive film is ruptured as a result of the emergence of slip steps through the passive film, and rapid dissolution of the crack tip occurs similar to the film rupture theory (184).
Table 1 (Continued)

**Brittle Film Theory**

The crack propagation occurs by repeated formation and rupture of a brittle film which grows into the metal at the crack tip (185).

**Corrosion Product Wedging Theory**

The buildup of corrosion products in existing cracks exert a wedging action and causes crack propagation (186).

**Tunnel Theory**

The crack propagates by formation of deep pits or tunnels via dissolution, followed by linking of these pits and tunnels by ductile rupture (187).
According to Ford (155, 156), there has been confusion regarding which mechanism operates in a given alloy/environment system, since the effect of many of the metallurgical variables on SCC can be explained by either the non-equilibrium hydrogen-transport theory or by the strain-assisted active path mechanisms. For example, coplanar dislocation morphologies will accelerate hydrogen transport as well as facilitate oxide rupture. The uncertainty in definition of the environment, composition, and potential at the crack tip, makes it difficult to delineate the operative mechanism. Parkins (171) has proposed that the controlling factors in the various mechanisms form a spectrum of interrelated effects, and a change of system variables may change the operative mechanism, or situations may exist where two mechanisms may operate simultaneously. The various mechanisms may have the same rate-determining steps.

2.10 Understanding SCC in Terms of Thermodynamics and Kinetics

The following presentation is described in detail by Ford (155, 156).

2.10.1 Thermodynamic Considerations

To determine which mechanism operates for a given alloy/environment the thermodynamic requirements for that mechanism must be satisfied. But for most cases in the ductile alloy/aqueous environment, both the dissolution-based and hydrogen-embrittlement-related theories are possible. This is due to the uncertain definition of the potential and environment at the crack tip, and the non-equilibrium considerations.
associated with hydrogen-transport mechanisms.

2.10.1.1 Thermodynamic Requirements for Dissolution-Based Theories.

Dissolution must be thermodynamically possible at the crack tip and at the same time a passive film must also be thermodynamically stable at the crack sides. In this manner a high aspect ratio crack can propagate (206). These conditions can be satisfied only in certain potential/pH combinations, where a passive film is thermodynamically stable but, if ruptured, a soluble species is metastable.

To calculate the stress intensity required to initiate crack propagation, an energy balance argument has been used in which the elastic strain-energy release rate and the chemical-energy change (due to dissolution at a continuously bared crack tip) are summed, and equated to the increase in system energy. The system energy increases due to changes in total surface energy and plastic energy accompanying an incremental increase in crack length (188). Such calculations have shown that dynamic straining, as in SSRTs, which forces the crack tip towards a continuously bared condition, causes a monotonic lowering of the stress intensity above which crack propagation occurs.

2.10.1.2 Thermodynamic Requirements for Hydrogen-Embrittlement-Related Theories

The environmental requirement in aqueous corroders is that hydrogen ions be reduced to hydrogen adatoms at the crack tip, as defined on the pH/Potential Pourbaix diagram. To calculate the stress
intensity required to initiate crack propagation, the stress conditions required to achieve a critical hydrogen concentration beneath the film-free crack surface are considered. This is done by using the thermodynamic relationship between the equilibrium hydrogen solubility and the dilational stress in front of the crack tip (189). The deformation kinetics theory (190), and the variations in surface energy terms (191) are also considered, to calculate the stress intensity required to initiate crack propagation.

2.10.2 Kinetic Considerations

Figure 17 (155) shows the schematic subcritical crack propagation rate as a function of the stress intensity. It shows that the stress-dependent Stage I cracking is related to the increasing plastic strain rate, the associated oxide rupture rate, and/or dislocation-aided hydrogen transport rate. It also shows that the stress-independent Stage II cracking is related to a change in the rate-controlling step to the liquid diffusion processes associated with either removing solvated cations from the crack tip or introducing solvated water molecules to the crack tip.

It was shown in the last subsection that, both the dissolution-based and hydrogen-embrittlement-related theories apply to the ductile alloy/aqueous environment systems. Therefore, they would have similar rate-controlling steps, with changes in the crack propagation rates reflecting changes in the rate controlling steps rather than the specific atom-atom rupture processes themselves.

The common interrelated steps of these two theories are shown in
Typical, subcritical crack propagation rate versus stress intensity relationship. Stress intensity $K$, is defined as:

$$K = A \sigma \sqrt{\frac{A}{B}}$$

where $\sigma$ = total tensile stress
$C$ = crack length
$A$, $B$ = geometrical constants

Figure 17 Schematic diagram of subcritical crack propagation rate as a function of stress intensity (155)
Figure 18 (155). For a given potential, pH, and anion content, both theories will be dependent on passivation, oxide rupture and liquid diffusion rates. This is because these rates will determine the charge passed per unit time in the dissolution-based theory, and the hydrogen adatom coverage and subsequent hydrogen permeation rate in the hydrogen-embrittlement-related theories.

2.10.2.1 Passivation Rate

It is well known that maximum SCC susceptibility with high aspect ratio cracks occurs at intermediate passivation rates, because 1) slow passivation rates following oxide rupture give excessive dissolution both at the crack tip and crack sides leading to crack blunting and arrest, and 2) fast passivation rates will minimize the amount of crack tip penetration per oxide rupture event (192). Based on this concept, cracking susceptibility in poorly passivating systems will increase by factors which promote passivation, and it will be maximum in potential ranges adjacent to active/passive transitions on a polarization curve. In strongly passivating systems cracking susceptibility will increase in the presence of aggressive anion and potential conditions, both of which lead to the breakdown of passivity. In the hydrogen-embrittlement-related theories which generally apply to cracking at cathodic potentials, the hydrogen-adatom coverage at the crack tip and subsequent absorption rate will depend on the passivation rate.

The understanding of the crack tip passivation rate on the kinetics of crack propagation can be applied to take remedial actions, develop analytical methods for determining the potential ranges of maximum SCC
Figure 18 Proposed interaction paths between the modes and mechanisms of SCC in ductile alloy/aqueous environment systems and the various rate controlling steps in crack propagation. Solid lines denote primary interactions, dashed lines denote secondary interactions (155)
susceptibility, and predict whether SCC will occur.

2.10.2.2 Oxide Rupture Rate

Oxide rupture at the crack tip is required for crack propagation by both the dissolution-based and hydrogen-embrittlement-related theories. Brittle films and metallurgical variables which favor planar slip morphologies facilitate oxide rupture. Following an oxide rupture event, the reaction kinetics at the crack tip can be used to relate the average crack propagation rate \( V \), by dissolution-based theories, to the oxidation charge density as follows:

\[
V = \frac{M}{nQ_f} \cdot \frac{Q_f}{t_f} = \frac{M}{nQ_f} \cdot \frac{Q_f}{t_f} \cdot \dot{i}
\]

where:

- \( M, Q \) = atomic weight and density of the metal respectively,
- \( F = \) Faraday's constant,
- \( n = \) number of electrons involved in the overall oxidation of a mole of metal,
- \( Q_f = \) oxidation charge density passed before the oxide is ruptured again,
- \( t_f = \) oxide rupture periodicity,
- \( \epsilon_f = \) fracture strain of the oxide at the crack tip, and
- \( \dot{i} = \) strain rate at the crack tip.

It is seen that the crack propagation rate increases with the crack tip strain rate. However, either plastic crack blunting by excessive plastic deformation on the crack sides at high strain rates or chemical crack blunting by excessive general corrosion on the crack sides can
limit the validity of the following relationship:

\[ V = A t^N \]  

[37]

So a critical crack tip strain rate exists at which the crack tip penetration overcomes the general corrosion on the crack sides (193).

2.10.2.3 Liquid Diffusion Rate

At high crack tip strain rates when the crack propagation rate is high, the need for entry of reactants (water or hydrogen ions) or the removal of products (solvated cations), makes liquid diffusion rate the rate-controlling step. But at low crack tip strain rates, passivation rate or oxide rupture rate is the rate-controlling step. Liquid diffusion rate is the rate-controlling step during the Stage II propagation shown in Figure 2-20. Ford (155), who investigated a low alloy steel/caustic system, found that the change in activation enthalpy from \(-20\) to \(4\) kcal/g mole that arises due to an increase in strain rate, corresponds to a change in the rate-controlling step from passivation rate to liquid diffusion rate. The theoretical quantification of the liquid diffusion rate is still unclear, even though it plays a dominant role in the crack propagation rate.

2.11 Factors Affecting SCC

It is well known that the required conditions for SCC are: 1) a susceptible metallurgical condition (sensitized microstructure), 2) specific environmental conditions, and 3) a critical level of stress (4). In this section the effect of metallurgical, environmental and stress factors, on SCC of austenitic stainless steels will be discussed.
2.11.1 Metallurgical Factors

The effect of various metallurgical factors: chemical composition, microstructure, DOSS, cold work, nonmetallic inclusions, surface condition and oxide films on SCC of austenitic stainless steels will be discussed in this section. The effect of nitrogen will first be discussed in detail in the subsection on the effect of composition.

2.11.1.1 Effect of Chemical Composition (Nitrogen in Particular)

There are numerous investigations on the effect of nitrogen on TGSCC of austenitic stainless steels in boiling MgCl₂ solutions, referred to as chloride cracking [10-21]. These indicate that nitrogen is detrimental to SCC resistance even at levels as low as 0.03 wt.% as shown in Figure 19 [195]. This detrimental effect is pronounced in AISI 304 stainless steels which have about 8 wt.% nickel and higher carbon contents as shown in Figure 20 [194].

The detrimental effect of nitrogen has been explained in terms of both microstructural and electrochemical reasons. Swann suggested that nitrogen causes dislocation coplanarity and planar glide leading to TGSCC to occur as shown in Figure 21 [15]. It is also known that nitrogen restricts cross slip and therefore promotes planar dislocation glide rather than cellular dislocation tangles [17]. The reason for the above observations is the effect of nitrogen on either decreasing the stacking fault energy (SFE) of austenitic stainless steels [15,195-197] as shown in Figure 21 [197], or forming a short range ordered (SRO) lattice with chromium (i.e. once SRO is destroyed, it is energetically
Figure 19 Detrimental effect of nitrogen on TGSCC of austenitic stainless steels (195)
Figure 20 Detrimental effect of nitrogen on TGSCC of AISI 304 SS which has 8 and 23 wt.% nickel and 0.02 and 0.06 wt.% carbon contents (194)
Figure 21 Effect of nitrogen and nickel on decreasing the SFE of austenitic stainless steels (197,15)
favorable to continue slip on the same slip plane rather than to reinitiate slip on other planes) as shown in Figure 22 (15,17). However, experimental evidence for the latter is lacking and limited evidence for SRO lattice has been observed only above 0.5 wt.% nitrogen (194). Stress aging phenomenon (16,198), which involves segregation of solute anions to active slip planes containing a high density of dislocations, produces the chemical inhomogeneity necessary to initiate and propagate a stress corrosion crack, as shown in Figure 23 (16). It shows that there is a correlation between the temperature ranges corresponding to the rapid decrease in cracking time and the rapid increase in the stress aging effect or interstitial effects. The effect of nitrogen on the passive film (199) has also been used to explain the detrimental effect of nitrogen on TGSCC.

It has however been shown that nitrogen is beneficial in high purity vacuum melted austenitic stainless steels (200). Although new grades of austenitic stainless steels with carbon levels reduced to prevent IGC and SCC, and with nitrogen additions to improve strength, have been proposed as alternative materials for BWR piping (15,35-39); there has been no systematic investigation on the effect of nitrogen on IGSCC of austenitic stainless steel in high temperature aqueous environments. The effect of nitrogen on SCC of AISI 304 SS in simulated BWR environments is studied in the present investigation, and the experimental results and analysis, discussion, summary and conclusions of this investigation will be described in detail in the following chapters.

At this stage it is worth pointing out that nitrogen has been found
Figure 22 Effect of nitrogen on forming a short range ordered lattice with chromium (17)
Figure 23 Effect of nitrogen and nickel on SCC, and the correlation between SCC and stress aging effect (16)
to be beneficial for pitting corrosion resistance of austenitic stainless steels (201-205). Various mechanisms have been proposed to explain this beneficial effect:

1) nitrogen consumes protons when it dissolves in the pitting solution, and prevents the lowering of pH in the early stage of pit formation, thus helping passivation of the pit before it becomes large (201),

2) nitrogen forms a metal nitride which co-exists with and strengthens the chromium oxide film on the stainless steel surface (203),

3) nitrogen segregates to the metal surface during preferential dissolution of metal atoms, leading to interfacial nitrogen enrichment on the metal side of the metal-film interface (205). Since there is direct experimental evidence (205), for interfacial nitrogen enrichment using Auger electron and x-ray photoelectron spectroscopy, this mechanism is most probable.

The effect of most elements except carbon, phosphorus and sulphur, on IGSCC of austenitic stainless steel in high temperature aqueous environments has not been investigated. Carbon has been found to be detrimental because it increases the DOS. Phosphorus and sulfur are also detrimental because they segregate to the grain boundary (22). However, the effect of most elements on SCC of austenitic stainless steel to chloride cracking have been investigated, but the mechanisms involved in most cases have not been well understood, except for the fact that in general austenite stabilizers are detrimental and ferrite stabilizers are beneficial. Carbon, chromium and molybdenum show minima in SCC
resistance (195,206). Nickel is beneficial because it increases the SFE of austenite as shown in Figure 21 (15,195). The effect of silicon is beneficial, manganese, sulfur, and boron are variable, and phosphorous, titanium, and niobium are detrimental (195).

2.11.1.2 Effect of Microstructure

With regard to chloride cracking of austenitic stainless steel, the effect of delta ferrite is beneficial because it stops the propagation of cracks across the austenite matrix. The presence of martensite which is produced as a result of plastic deformation during cold working is also beneficial in a similar way (206). Sigma phase and sulfide inclusions seem to have no effect, except for initiating the cracks at the inclusions (206,207). The effect of increasing grain size is detrimental because of more slip and easy initiation of the crack at the metal surface (208). Ruther et.al. (33) have shown that different carbide morphologies and distributions in sensitized austenitic stainless steels are equally detrimental to IGSCC in high temperature aqueous environments. It is well known that a sensitized microstructure is responsible for IGSCC of austenitic stainless steel in high temperature aqueous environments and this is discussed in the next subsection. In the present investigation, the correlation between sensitized microstructure and IGSCC susceptibility was studied, which will be presented in the subsequent chapters.

2.11.1.3 Effect of DOS

The effect of DOS on IGSCC of austenitic stainless steel in high
temperature aqueous environments has been studied by various investigators (22,25,30-32). Smialowska and Cragnolino (22) state in their review paper that although various investigations have shown that the susceptibility to IGSCC increases with increasing sensitization, there is no quantitative definition of the critical DOS necessary to cause IGSCC, in spite of efforts to correlate the DOS measured using EPR tests to SCC susceptibility tests. Ruther et al. (33) suggest that while EPR tests are sensitive to the width of the chromium concentration profile across the grain boundary, initiation of SCC is more sensitive to the depth than to the width. Poznansky and Duquette (31) also suggest that the depth of the chromium concentration profile is important, and that it determines the potential at which: 1) SCC initiates and 2) breakdown of passivity occurs. This suggestion (31,33) that the minimum chromium concentration at the grain boundary is more important than the width of chromium depletion, is in contrast to Andrenen's (16) earlier suggestion that the width is more important. In the present investigation the steels with different nitrogen and carbon levels had different DOS, and its effect on IGSCC, and the correlation of the microchemistry at the grain boundary to IGSCC susceptibility in high temperature aqueous environments, will be shown in an attempt to resolve the existing contradiction.

2.11.1.4 Effect of Cold Work

The effect of cold work on IGSCC of austenitic stainless steel in high temperature aqueous environments has been reviewed by Smialowska and Cragnolino (22), in which they report that cold work is deleterious.
This is due to the presence of deformation-induced martensite and the effect of cold work on sensitization. Low amounts of cold work cause rapid nucleation and growth of carbides and increase susceptibility to IGSCC; while at high amounts of cold work diffusivity of chromium increases and there are no continuous chromium depleted regions, thus increasing IGSCC resistance.

2.11.1.5 Effect of Nonmetallic Inclusions

The effect of nonmetallic inclusions is reflected by the heat to heat differences and tensile axis orientation dependence of the susceptibility of AISI 304 SS to IGSCC. The presence of various types and levels of impurities, and differences in the microstructure, composition, size and shape of nonmetallic inclusions give rise to heat to heat differences in IGSCC susceptibility. The presence of nonmetallic inclusions and precipitates which are elongated in the rolling direction gives rise to lower IGSCC susceptibility in samples with their tensile axis oriented parallel to the rolling direction (longitudinal) than compared to the transverse direction (22).

2.11.1.6 Effect of Surface Condition and Oxide Films

Smialowska and Cagnolino (22) report that nucleation of IGSCC occurs more easily on rough than on smooth metal surfaces, and large defects on the metal surface, like crevices and notches, accelerate cracking. Andresen's (25) study showed that surface condition affects crack initiation. He (25) showed that shot peening and presumably any treatment which inflicts cold work on the surface promotes SCC.
initiation from mechanical shear cracks, and the SCC phenomenon becomes
initiation limited. Solomon's (32) study showed that while in
electropolished samples only one stress corrosion crack grows until it
causes failure, in as-machined, grit blasted, and acid pickled samples
multiple stress corrosion cracks are observed.

Smialowska and Cragnolino (22) state in their review paper that the
data on the composition and structure of oxide films occurring at
different temperatures are different. This is attributed to the
differences in surface condition, heat and/or mechanical treatments,
concentration of dissolved oxygen, and time of heating. They concluded
that films formed at temperatures lower than 200°C grow according to a
logarithmic law, reach a limiting thickness, and are protective.
However, films formed at temperatures higher than 200°C grow faster, are
thick, and less protective. It has been reported that at temperatures
lower than 200°C, chromium in austenitic stainless steel produces an
amorphous and compact passive film, which is enriched by nickel,
molybdenum and nitrogen (205,209), whereas at temperatures higher than
200°C, a thicker film forms on grain boundaries compared to the grains
of sensitized AISI 304 SS (210).

2.11.2 Environmental Factors

The effect of various environmental factors: potential, water
impurities, dissolved oxygen content, temperature, pH, and fluid flow on
SCC of austenitic stainless steel in high temperature aqueous
environments will be discussed in this sub-section.
2.11.2.1 **Effect of Potential**

Smialowska and Cragnolino (22) describe in their review paper the relevance of potential to IGSCC susceptibility. Corrosion potential is related to the dissolved oxygen content; potentials of $-0.6 \ V_H$ to $-0.72 \ V_H$ correspond to less than 10 ppb oxygen, which was the level aimed in this investigation. Potentials around $0 \ V_H$ correspond to about 1 ppm oxygen. The corrosion potential decreases with increasing temperature. The corrosion is controlled by the reduction of hydrogen ions at low oxygen contents, and by the reduction of oxygen at high oxygen contents. They (22) also state that, because the susceptibility to IGSCC is related to the dissolved oxygen content, which is in turn related to the corrosion potential, there are attempts to investigate IGSCC susceptibility under applied potential conditions in dilute sodium sulfate aqueous solutions, assuming that sulfate anions will not influence the SCC phenomenon. Cragnolino et.al. (23) and Lin et.al. (24) studied SCC susceptibility of AISI 304 SS as a function of applied potential in deaerated 0.01M Na$_2$SO$_4$ and 0.01M NaCl at 250°C (the same environment used in the present investigation). Their (23) results are shown in Figure 24, in which it is seen that IGSCC occurs at potentials above a critical potential, which is around $-0.3 \ V_H$ and depends on DOS. In the present investigation, the effect of applied potential on SCC susceptibility of AISI 304 SS containing nitrogen and the relation between the critical potential and DOS will be presented in the subsequent chapters. This aspect is of great technical importance for the operation of the BWR, because it has been reported that hydrogen injected into the BWR modifies the water chemistry and decreases the
Figure 24 Effect of applied potential on SCC susceptibility
corrosion potential to below the critical potential for IGSCC, and thus eliminates the occurrence of IGSCC (34, 211, 212). Another aspect which needs clarification is the role of potential versus dissolved oxygen, since some investigators (33) emphasise the latter, and others (215) the former. It is hoped that the present investigation will clarify this aspect.

2.11.2.2 Effect of Water Impurities

Cragnolino and Macdonald (213) state that ionic impurities like Cl\(^{-}\), SO\(_4\)\(^{2-}\), etc, which are produced or released as trapped impurities by thermal and/or radiolytic decomposition of cationic resins, enhance the susceptibility of AISI 304 SS to IGSCC. The effect of water impurities on IGSCC susceptibility has been investigated by various investigators (22-24, 28-31, 33, 211, 213-216). Hishida and Nakada (214) have shown that Cl\(^{-}\) levels of as low as 0.2 to 1 ppm causes IGSCC of a slightly sensitized steel in high temperature water containing high dissolved oxygen; however even Cl\(^{-}\) levels of 100 ppm did not influence SCC when low dissolved oxygen was present. The chloride and oxygen levels necessary for IGSCC to occur have been plotted by Gordon (215) as an oxygen-chloride plot. Poznansky and Duquette (30) explained the effect of Cl\(^{-}\) and SO\(_4\)\(^{2-}\) on IGSCC susceptibility, based on a dissolution controlled mechanism, considering the effect of Cl\(^{-}\) and SO\(_4\)\(^{2-}\) on the repassivation rate. Andresen and Indig (27) showed that additions of Na\(_2\)SO\(_4\) and H\(_2\)SO\(_4\) greatly increased the susceptibility to IGSCC; they explained this in terms of its effect on shifting the corrosion potential to higher values as a result of active corrosion. Cragnolino
and Macdonald (213) showed that sensitized AISI 304 SS is susceptible to IGSCC in high temperature \( \text{Cl}^-, \text{SO}_4^{2-}, \text{B(OH)}_4^-, \) and \( \text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-} \) aqueous solutions above a critical potential (which is dependent on the temperature and solution composition). They (213) also showed that the critical potential is above the corrosion potential, measured in deaerated solutions, and decreases linearly with increasing temperature. However Ruther et al. (33) explain the deleterious effect of the anionic impurities in terms of their effect on decreasing the pH and increasing the conductivity of the reactor water. The present investigation in which SCC studies have been performed in deaerated \( \text{SO}_4^{2-} \) and \( \text{Cl}^- \) solutions, under applied potential conditions, will help understand which of the various mechanisms mentioned above is operative.

2.11.2.3 Effect of Dissolved Oxygen Content

The effect of dissolved oxygen content has been investigated by various authors (22, 25, 26, 28, 29, 33, 215, 217, 218). Hishida and Nakada (217) showed that dissolved oxygen accelerated IGSCC of sensitized AISI 304 SS in high temperature water. Ford and Povich (217) have shown that crack propagation rates increase at dissolved oxygen contents above 0.1 ppm. Smialowska and Cragolino (22), and Andresen (25), have constructed a dissolved oxygen-temperature diagram, which shows what combinations of dissolved oxygen and temperature give rise to SCC. They point out that below 0.1 ppm dissolved oxygen TGSCC occurs in SSRTs performed in high temperature water. A mechanism for IGSCC due to dissolved oxygen has been proposed by Fujiwara et al. (26); when the dissolved oxygen is low, IGSCC does not occur because the corrosion potential of the steel is
less noble, the growth rate of the surface film on the steel is low, and the film is elastic and repaired easily if it breaks. However when dissolved oxygen is sufficient, IGSCC occurs because the corrosion potential of the steel is noble, and a thick surface film forms. If tensile stresses are high the film breaks, the cracked part of the film acts as a crevice, the pH of the solution in the crevice decreases, and this acidified solution attacks the chromium depleted zone along grain boundaries. Hirano et al. (29) also use a similar mechanism as above, but they also consider the effect of oxygen on the composition of the oxide film; they showed that when dissolved oxygen is sufficient, IGSCC occurs because when the oxide film is ruptured, the grain matrix recovers but not the grain boundaries.

2.11.2.4 Effect of Temperature

The effect of temperature has been studied by various investigators (22-25,218). Ford and Silverman (218) showed that IGSCC occurs even at 50°C, given the right temperature-oxygen-potential combination. Andresen (25) showed that SCC becomes initiation limited as temperature decreases, and the strain to initiation decreases with increasing temperature. Lin et al. (24) have constructed temperature-potential domains in which IGSCC, simultaneous IGSCC and TGSCC, and simultaneous IGSCC and pitting corrosion occur. The critical potential for IGSCC was equal to the pitting potential at temperatures lower than 150°C, but at higher temperatures it lies within the passive range of the alloy, and the potential for breakdown of passivity becomes independent of temperature and corresponds to the potential at which TGSCC occurs (24).
Cragnolino et al. (23) and Lin et al. (24), explained the effect of temperature on SCC behavior in terms of the different protective properties of the surface films formed at temperatures below and above 200°C, the films formed below 200°C being thin and protective, while the ones formed above 200°C being thicker and less protective. They also concluded that, based on the apparent activation energy for intergranular crack propagation in the temperature range 200 to 275°C, the rate determining step in the overall SCC process is the liquid diffusion rate. Such an interpretation is consistent with Ford's (219), who found the same value for the activation energy in a low alloy steel/caustic system which was under liquid diffusion rate control.

2.11.2.5 Effect of pH

Smialowska and Cragnolino (22) state in their review paper that, although it has been suggested that the susceptibility to IGSCC is enhanced by acidity, it seems that the critical potential for IGSCC is only slightly dependent upon pH in nearly neutral or weakly acidic solutions, due to lack of sufficient data. However, the recent investigation by Andresen (220) showed that the bulk pH affects initiation and failure strains, while increasing conductivity at neutral pH affects failure strains; i.e. crack initiation is more strongly influenced by changes in solution pH than conductivity in the neutral to acid pH range, which contrasts with the study of Ruther et al. (33) on the effect of either acidic or neutral impurity additions on accelerating crack propagation. Ruther et al. (33) have shown that impurities which decrease the pH and increase the conductivity cause
IGSCC. Andresen (220) explained his results in terms of the changes in the electronic and structural properties of the passive films that form on stainless steel at temperatures above 200°C; as a result of which the passive film does not act as a physical barrier to impurities, and it is the reaction at the metal-electrolyte interface that perhaps controls crack initiation.

2.11.2.6 Effect of Fluid Flow

Shim (221) has carried out a systematic study on the effect of fluid flow on the SCC of AISI 304 SS in high temperature aqueous solutions. Relative motion between a fluid and metal surface affects mass transport processes and influences general and localized corrosion. Generally high fluid flow velocity increases corrosion by supplying the corroders to the metal surface at a high rate, but it may also decrease corrosion by making the inhibitors more effective. Choi et al. (222) showed that IGSCC susceptibility decreases with increasing fluid flow velocity, because of the delay in crack initiation due to the agglomeration of loose corrosion products in weak spots on the metal surface. Shim (221) also found that increasing fluid flow velocity decreases IGSCC susceptibility, which was explained in terms of an increased repassivation rate of the film free site on the metal surface, and improvement in the protective properties of the film as fluid flow velocity increases. Fuller and Macdonald (223) have shown that fluid flow velocity has no effect on the critical potential for IGSCC.
2.11.3 Stress Factors

The effect of various stress factors: stress, strain, strain rate and stress intensity, and the three types of stresses in a welded pipe that contribute to occurrence of IGSCC in an operating BWR namely, welding residual stress, dynamic loading, and residual stress produced by surface grinding (58), will be discussed in this subsection.

2.11.3.1 Effect of Stress, Strain, Strain Rate and Stress Intensity

Smialowska and Cragnolino (22) have reviewed the effect of stress, strain and strain rate on SCC of AISI 304 SS in high temperature aqueous environments. The time to failure decreases with increasing stress, and at stress levels corresponding to the yield strength no SCC occurs in the constant deflection and constant load tests (224). In the SSRTs the minimum strain necessary to initiate intergranular cracks is about 5.5% (225). The role of strain in the SSRT is to promote repetitive film rupture which facilitates crack initiation and propagation (226). The strain rate that is used in the SSRT is very important, because if it is too high, ductile failure by void coalescence would occur before the necessary corrosion reactions that promote SCC could take place, and if it is too low, repassivation will occur resulting in crack arrest (226). At intermediate strain rates, when SCC is controlled by metal dissolution or mass transport, the crack velocity is independent of strain rate (22). For most systems a strain rate of $10^{-5}$ to $10^{-6}$ per second will promote SCC (227). The effect of stress intensity on intergranular crack growth rate has not been studied in detail. The few studies that have been reported, using fracture mechanics type
specimens, do indicate that a threshold stress intensity ($K_{ISCC}$) exists below which cracks will not propagate (228), and that the crack growth rate depends on the stress intensity factor ($K_I$) (213, 229-231). Cragno-lino and Macdonald (213) and Chung et al. (231) have showed that the crack growth rate increases with increasing $K_I$ up to 20-25 MPa.m$^{1/2}$, but it is almost independent of $K_I$ at higher values, and that a critical potential for IGSCC exists. They (213) attributed the initiation and propagation of intergranular cracks, after rupture of the passive film under stress, to anodic dissolution of the chromium-depleted regions along grain boundaries, accompanied by acidification at the crack tip produced as a consequence of the hydrolysis of metal cations.

2.11.3.2 Effect of Welding Residual Dynamic Loading and Surface Grinding Stresses

These are the three types of stresses that lead to IGSCC of BWR piping (58), the effect of which have been reviewed by Chung (3). The following presentation is based on his review. The combination of welding residual and applied stresses will result in promoting IGSCC. However, if the welding residual stress is compressive in the HAZ of the inside surface of the pipe, then resistance to IGSCC increases. Compressive stresses can be introduced by using newly developed better welding techniques and post weld heat treatment (induction heating stress improvement). It was mentioned earlier that at stress levels below the yield strength no SCC occurs, but White and Berry (232) observed IGSCC at stress levels below the yield strength under dynamic loading conditions, i.e. superimposing a cyclic load on a mean load.
Therefore, dynamic loading during BWR normal operating conditions and start-up contributes to the occurrence of IGSCC at stresses below the yield strength. Post-weld surface grinding introduces additional stresses, severe notch effects and a layer of heavily surface cold worked material, which can contribute to the initiation of IGSCC. Subsequent welding operations will introduce localized microstructural changes in this layer of surface cold work, which will cause IGSCC.

2.12 SSRT To Study SCC and Electrochemical Tests to Study Anodic Polarization Behavior

There are four important techniques used to study SCC (233):

1) Constant load or displacement tests on smooth specimens, to determine the threshold stress or the failure time at a given stress.

2) Precracked fracture mechanics specimens to determine $K_{ISC C}$ and the crack velocity as a function of $K_I$.

3) SSRTs to determine the normalized time or elongation to failure ratio.

4) Several electrochemical techniques to determine the range of potentials which cause SCC.

There have been attempts to correlate the susceptibility to IGSCC with the anodic polarization behavior of the stainless steel. Various investigators have measured the anodic polarization curves in high temperature aqueous environments. In this subsection the SSRT technique to study SCC is first presented, then electrochemical tests to study anodic polarization behavior are presented, and finally attempts to
correlate the SCC susceptibility and anodic polarization behavior are discussed.

2.12.1 SSRT to Study SCC

SSRT has been in use for nearly 20 years, and it is one of the most popular methods for studying SCC. It has more relevance than the rapid sorting test as which it was first used. Various investigators have used this technique to study the effect of a number of variables on SCC of sensitized AISI 304 SS in high temperature aqueous environments. In this test application of slow dynamic strain assists in stress corrosion crack initiation. The strain rate that is used is very important, because if it is too high ductile failure by void coalescence will occur before the necessary corrosion reactions that promote SCC can take place, and if it is too low repassivation will occur, resulting in crack arrest (226). For most systems a strain rate of $10^{-5}$ to $10^{-6}$ s$^{-1}$ will promote SCC (227). The role of strain in SSRT is to promote repetitive film rupture which facilitates crack initiation and propagation. While the mechanical factor is controlled by choosing an appropriate strain rate, the electrochemical factor is controlled by applying a constant potential to the straining electrode. Potential is an important variable since crack formation and propagation depend on a critical balance between activity and passivity at the crack tip, i.e. film rupture must produce sufficient dissolution to advance the crack, yet the crack sides must remain relatively passive; and only in a certain range of potential will this balance be achieved (226).

The SSRT is performed using plain tension specimens strained in
stiff frame machines. The corrosive environment is contained in autoclaves if high temperatures and pressures are used. The details of the experimental set up will be described in Chapter 4 on materials and experimental procedures. Criteria of cracking susceptibility are

(i) fracture mode, (ii) stress-strain curve recorded during the test, (iii) time to failure, % elongation at failure, reduction in area, fracture stress, maximum stress etc., all of which are generally normalized with respect to a test conducted in an inert environment, (iv) secondary cracks along the gage length, which provide useful parameters like crack length, crack velocity and crack frequency, (v) SCC susceptibility index,

\[ I_{SCC} = \frac{A_{SCC}}{A_{mech}} \quad [38] \]

where \( A_{SCC} \) and \( A_{mech} \) are the areas of SCC fractured surface and the mechanically fractured surface areas respectively, \( I_{SCC} \) can be derived from stress-strain curves and is given as:

\[ I_{SCC} = \frac{1 + \varepsilon_n \cdot P_n}{1 + \varepsilon_{n}^{SCC} \cdot P_{n}^{SCC}} - 1 \quad [39] \]

where \( \varepsilon_n \) and \( P_n \) are strain and load at maximum load respectively, in the load-elongation curves obtained in a noncorrosive environment; and \( \varepsilon_{n}^{SCC} \) and \( P_{n}^{SCC} \) the same obtained in a corrosive environment. The \( I_{SCC} \) obtained by both equations [38] and [39] have a linear correlation.

Comparison of SSRT results with other tests, like constant strain and load tests, show a good correlation. A disadvantage of the SSRT is that it does not give a stress intensity that can be used directly in design considerations. But its many advantages have been documented
and the relevance of the SSRT technique has been discussed by Ford (155, 156). While Ruther et al. (33) point out that the large plastic strains involved in the SSRTs are severe and are not characteristic of reactor loading conditions, Ford (155, 156) asserts that the SSRT is fundamentally a valid accelerated test for ductile-alloy/aqueous-environment systems, because it accelerates the rate-determining step (oxide rupture rate) without changing to a different rate-determining process, but this test is valid only when the crack sides are protected and crack blunting and arrest does not occur at a critical strain rate that is required for continued crack propagation. Ford (156) also points out that there is a danger in accelerating the propagation process to the extent that the rate-determining process changes from oxide rupture rate/passivation rate control to liquid diffusion rate control. Cragnolino and Smialowska (22) have pointed out that the large plastic strain involved in the SSRTs initiates transgranular stress corrosion cracks, which have no practical significance.

2.12.2 Electrochemical Tests to Study Anodic Polarization Behavior

There have been attempts to correlate the susceptibility to IGSCC with the anodic polarization behavior of the stainless steels. Various investigators have measured the anodic polarization curves for both solution annealed and sensitized AISI 304 SS in high temperature aqueous environments. These have been reviewed by Cragnolino and Smialowska (22). They state that significant differences in the shape of the polarization curves are observed, when comparing the results of
different authors, and correlation of these results is not easy because of the different types of reference electrodes employed by different investigators. They explain the differences in the shape of polarization curves measured by different authors in terms of differences in the experimental parameters, like heating rate of the autoclaves (oxides of different thickness can form), rate of potential scanning, and type of autoclave (in static autoclaves, oxidation and deposition of corrosion products can occur). They also report that the shape of the polarization curves for solution annealed and sensitized stainless steels are the same, but the latter show higher current densities. Indig and Vermilyea (236), and Kushiya et al. (237), have also reported this observation.

The anodic polarization behavior of the steel is different in sulphate and chloride solutions (22). In sulphate solutions transpassive behavior is exhibited after passive behavior, while in chloride solutions the breakdown of passivity occurs after passive behavior. It has been reported that alloys with lower chromium content show a larger current density in both the active and passive regions; with this effect being more pronounced at higher temperatures (22). Indig and Vermilyea (236) suggest that the resistance to IGSCC decreases with increasing potential, because of the increasing rate of anodic dissolution of the chromium depleted zones, and lowering of the pH in the vicinity of the corroding surface. But Smialowska and Cragnoino (22) conclude that it is neither possible to determine the critical potential for IGSCC initiation, nor the region of potentials at which SCC occurs, from the shape of the anodic polarization curves. In the present investigation the anodic polarization behavior of both solution annealed and
sensitized AISI 304 SS containing various levels of nitrogen, was studied in both high temperature aqueous sulphate and chloride solutions, to correlate it with IGSCC susceptibility. These results will be presented and discussed in the subsequent chapters.

2.13 Prevention of SCC

Parkins (4) has given an overview of prevention and control of SCC; he states that prevention and control procedures are divided into approaches based upon metallurgical, electrochemical (or environmental), mechanical (or stress) and operational aspects. He (4) states that metallurgical approaches involve modifications in the alloy composition, structure and grain size, including impurity control. For the BWR piping problem it has been suggested that reducing the carbon content and adding nitrogen to maintain the same strength level is effective (35-39), as is solution heat treatment of stainless steel to redissolve the carbides and eliminate chromium depletion at previously sensitized grain boundaries (238). Parkins (4) states that electrochemical or environmental control may be through the control of potential, inhibition, or the application of coatings, organic or metallic. For the BWR piping problem, it has been shown that injection of hydrogen into the BWR causes the dissolved oxygen to decrease, which results in a drop of the corrosion potential to below that at which IGSCC could be expected (34,211,212); and also metal cladding on the inside of the BWR pipe weld ends prevents IGSCC, because the metal cladding consists of a duplex structure, and the ferrite in it arrests the propagating stress corrosion cracks (4). Parkins (4) states that control of stress factors
involves control of residual stresses, full or partial thermal stress relief, and introduction of compressive stresses into the surface, where cracks might otherwise initiate. For the BWR piping problem, thermal stress relief by induction heating the outside of the pipe to 500-550°C, while maintaining the inside surface at 100°C with cooling water, results in compressive stresses on the inside surface where SCC may occur in service (4). Similar changes in the residual stress distribution are achieved by special welding techniques (4). Parkins (4) states that the control of operational factors are minimization of stress changes or cyclic loading and the reduction of temperature. For the BWR piping problem it is well known that the most damaging stress fluctuations are likely to be associated with start-up and shut-down, and deaeration or other procedures during start-up and shut-down can prevent the occurrence of IGSCC (4). In the present investigation the effect of alloy composition, the reduction of carbon and addition of nitrogen, on sensitization and SCC of BWR piping material in simulated BWR environments is studied to solve this problem.
Chapter III

THEORETICAL MODELING OF SENSITIZATION

The relevant literature on thermodynamic and kinetic modeling of sensitization was presented in subsection 2.4. In subsection 3.1, a thermodynamic model of sensitization based on the model of Stawstrom and Hillert (46) and the approaches of previous investigators (47-49, 77) will be presented. The thermodynamic model can be used to calculate TTS diagrams and $X_{\text{Cr}}^j$, and the effect of nitrogen is incorporated into the model by using the free energy interaction coefficients of nitrogen on chromium and carbon. In subsection 3.2, the kinetic model suggested by Zener (81) will be presented. The kinetic model can be used to calculate chromium concentration profiles perpendicular to the grain boundaries, and the effect of nitrogen is incorporated into the model by using the appropriate value of the diffusion coefficient of chromium in austenite, which is a function of nitrogen and carbon content. In subsection 3.3, the mathematical model suggested by Hall et. al. (90) will be presented. The mathematical model can be used to consider the effect of electron beam broadening on AEM measurements.

3.1 Thermodynamic Modeling of Sensitization

This section outlines the thermodynamic analysis that has been used to calculate the TTS diagrams and $X_{\text{Cr}}^j$. 
Stawstrom and Hillert (46) have considered the precipitation of \( \text{Cr}_2\text{C}_6 \) based on diffusion control of chromium in austenite. To describe the early stages of precipitation they derived the equation:

\[
t = \frac{m^2}{4D} \left( \frac{x_{\text{Cr}}^\circ - x_{\text{Cr}}^i}{0.13 - x_{\text{Cr}}^i} \right)^2
\]

where:

\[ t \] = time in seconds for sensitization to start at a given temperature \( T \) in °K.

\[ m \] = width of the chromium depleted zone, i.e. regions with mole fraction of chromium less than 0.13, adjacent to the grain boundaries when sensitization starts which is estimated to be 200 °A.

\[ D \] = diffusion coefficient of \( \text{Cr} \) in austenite \( = 0.08 \exp(-58500/RT) \) cm²/sec.

\[ R \] = gas constant \( = 1.9 \text{ cals/°K mole.} \)

\[ x_{\text{Cr}}^\circ \] = mole fraction of \( \text{Cr} \) in the bulk which is obtained from the composition of the steel.

\[ x_{\text{Cr}}^i \] = mole fraction of \( \text{Cr} \) at the carbide-austenite interface.

\[ x_{\text{Cr}}^i \] is determined using the method of Tedmon et al (47). The reaction:

\[
23\text{Cr} + 6\text{C} \xrightarrow{\text{equilibrium}} \text{Cr}_2\text{C}_6
\]

is considered to be in equilibrium at the carbide-austenite interface. Hence:

\[
\Delta G_f^\circ (\text{Cr}_2\text{C}_6) = -RT \ln K
\]
where $\Delta G_f^o(Cr_{23}C_6)$, the free energy of formation of $Cr_{23}C_6$, is given (239) by:

$$\Delta G_f^o(Cr_{23}C_6) = -9.828 \times 10^{-4} - 9.241 \text{ cals/mole} \quad [43]$$

and the equilibrium constant, $K$, is

$$K = \frac{1}{(\gamma_C \gamma_{Cr}^2)^{23}(\gamma_C \gamma_{Cr}^6)} \quad [44]$$

where $\gamma_C$ is the mole fraction of carbon in the steel obtained from the steel composition. In view of the fact that the diffusion coefficient of carbon is about 7 orders of magnitude higher than that of chromium, there would be an even carbon activity in the whole material. $\gamma_C$ is the activity coefficient of carbon. $\gamma_C$ can be calculated using the formulation of Natesan and Kassner (240), which was modified to account for the effect of nitrogen by introducing an additional term $U_N^C X_N$:

$$\ln C = \ln(\frac{1}{1-X_C}) + U_0 + U_C \left(\frac{X_C}{1-X_C}\right)$$

$$+ U_{Ni} X_{Ni} + U_{Cr} X_{Cr} + U_{Cr}^1 X_C^2 + U_N^C X_N$$

[45]

where the parameters $U_i$, $U_{Cr}^1$ and $U_N^C$ are temperature dependent constants, and $X_i$ is the mole fraction of component $i$.

The activity coefficient of chromium as suggested by Pullman (48), $\gamma_{Cr}^F$, can be calculated using the following equations [46-50] (48, 241, 242) and the data of Kaufman and Nesor (243) on the Fe-Cr-Ni system.

$$E_{G_{ij}} = x_i^*g_i + x_j^*g_j + x_i X_i (g_{ij} X_i + g_{ji} X_j)$$

[46]

where $E_{G_{ij}}$ is the excess free energy of solution of each binary pair
\[ E_G = x_i x_j E_{G_{ij}} \left( \frac{x_i}{x_i + x_j}, \frac{x_j}{x_i + x_j} \right) + x_i x_k E_{G_{ik}} \left( \frac{x_i}{x_i + x_k}, \frac{x_k}{x_i + x_k} \right) \]
\[ + x_j x_k E_{G_{jk}} \left( \frac{x_j}{x_j + x_k}, \frac{x_k}{x_j + x_k} \right) \]  

[47]

\[ E_{G_i} = E_G + \frac{dE_G}{dx_i} - \sum x_i \frac{dE_G}{dx_i} \]  

[48]

\[ \gamma_{Cr}^F \] is estimated using equation [49]

\[ E_{G_{Cr}} = \xi_{kn} + \gamma_{Cr} + \frac{x_{Fe}}{(x_{Cr} + x_{Fe})^2} \left[ x_{Cr}(x_{Cr} + 2x_{Fe})g_{CrFe} + x_{Fe}^2 g_{FeCr} \right] \]
\[ + \frac{x_{Ni}}{(x_{Cr} + x_{Ni})^2} \left[ x_{Cr}(x_{Cr} + 2x_{Ni})g_{CrNi} + x_{Ni}^2 g_{NiCr} \right] = RT \ln \gamma_{Cr}^F \]  

[49]

where

\[ \xi_{kn} = - \left[ \frac{x_{Fe} x_{Cr}}{x_{Fe} + x_{Cr}} \left( x_{Fe} g_{FeCr} + x_{Cr} g_{CrFe} \right) + \frac{x_{Fe} x_{Ni}}{x_{Fe} + x_{Ni}} \left( x_{Fe} g_{FeNi} + x_{Ni} g_{NiFe} \right) \right. \]
\[ + \left. \frac{x_{Cr} x_{Ni}}{x_{Cr} + x_{Ni}} \left( x_{Cr} g_{CrNi} + x_{Ni} g_{NiCr} \right) \right] \]  

[50]

An additional term \( U_{Cr}^N \) \( x_N \) was included in the equation to calculate \( \gamma_{Cr}^F \), on top of that calculated using Fullman's approach, \( \gamma_{Cr}^F \).
\[ \ln \gamma_{Cr} = \ln \gamma_{Cr}^F + U_{Cr}^N \chi_N \]  

where \( U_{Cr}^N \) is a temperature dependent constant. The temperature dependence of both \( U_C^N \) and \( U_{Cr}^N \) were considered as suggested by Lupis (244):

\[ U_{Cr}^N = \frac{\sigma_N^i}{RT} - \frac{\eta_N^i}{R} \]  

where \( \sigma_N^i \) and \( \eta_N^i \) are enthalpy and entropy interaction coefficients respectively. The values of \( U_C^N \) and \( U_{Cr}^N \) are given by Lupis (245) as follows:

\[ U_C^N = 11315.8/T - 0.3449 \] \[ U_{Cr}^N = -36736.8/T + 9.6140 \]

All the variables in equation (40) can thus be calculated and \( t \) can be determined. The FORTRAN program to do these computations written for the VAX 11/780 computer is shown in Appendix A.

3.2 Kinetic Modeling of Sensitization

The kinetic model is based on bulk diffusion controlled growth of a precipitate into the lattice proposed by Zener (81) and modified by various investigators (82-84). Hall and Briant (49) applied it to the growth of \( \text{Cr}_{23}\text{C}_6 \) into the austenite lattice. The basic diffusion equation to be solved is:

\[ \frac{dC(r,t)}{dt} = D \nabla^2 C(r,t) \]  

[55]
where \( C(r,t) \) is the position \( r \) and time \( t \) dependent chromium concentration, and \( D \) is diffusion coefficient of chromium in austenite.

The solution to the above partial differential equation, is obtained using the boundary conditions that \( C(r,0) = C_m \), ie at time \( t = 0 \), the concentration at all points is \( C_m \), the bulk chromium concentration; and \( C(r_i,t) = C_i \), ie. the concentration at the carbide-austenite interface at a carbide of radius \( r_i \) is \( C_i \). The solution is given as:

\[
C(r,t) = C_m + \frac{\exp \left( -\frac{r^2}{4Dt} \right)}{\sqrt{\pi \frac{r}{2D}}} \left[ 1 - \text{erf} \left( \frac{r}{\sqrt{2Dt}} \right) \right] + \frac{\exp \left( -\frac{r_i^2}{4Dt} \right)}{\sqrt{\pi \frac{r_i}{2D}}} \left[ 1 - \text{erf} \left( \frac{r_i}{\sqrt{2Dt}} \right) \right]
\]

The values for \( C_i \) and \( D \) that will be used in the computations will be that obtained experimentally using the AEM. In this manner the effect of nitrogen is incorporated into the kinetic model. The FORTRAN program to do these computations written for the VAX 11/780 computer is shown in Appendix B.

3.3 Mathematical Modeling of Electron Beam Broadening

The agreement between the measured and calculated chromium concentration profiles can be improved by considering the broadening of the electron beam as it passes through the sample. The effect of beam broadening has been estimated analytically by previous investigators (90-94). In this approach the electron beam intensity distribution through the thickness of the foil and the concentration profile across the grain boundary are considered to be Gaussian functions:
\[ I(\text{xyz}) = A(z) \exp\left[-\frac{(x^2+y^2)}{(\rho(z))^2}\right] \] \[ C(\text{xyz}) = C_0 \exp\left[-\frac{(x-x)^2}{\alpha^2}\right] \]

where the geometry considered is shown in Figure 25 (90); \( I(\text{xyz}) \) is the electron intensity at any point in the foil, \( Q(z) \) and \( A(z) \) are the half width and height of the Gaussian at depth \( z \) in the foil, \( C(\text{xyz}) \) is the chromium concentration at any point, \( C_0 \) the matrix chromium concentration, \( \alpha \) is the half width and \( X \) the distance between the probe center and the grain boundary.

Application of the principles that lead to the Cliff-Lorimer relation for thin foils relates the X-ray intensity to the concentration, and if the electron beam broadening is considered to be given by the single scattering model, we can calculate the concentration:

\[ C(\text{xyz}) = C_0 \frac{F(X)}{t} \] \[ F(X) = \int_0^t \frac{\alpha}{[\rho(z)]^{2+\alpha^2}^{1/2}} \exp\left(-\frac{x^2}{[\rho(z)]^{2+\alpha^2}}\right) dz \]

\[ \rho(z) = \beta z^{3/2} + \beta_0 \]

\[ \beta = 3.125 \times 10^5 (Z/E_0)(P/A)^{1/2} \]

where \( \beta_0 \) is the half width of the incident probe, \( Z \) is the atomic number, \( E_0 \) is the electron energy in electron-volts, \( A \) is the atomic weight and \( \rho \) is the density in g/cm\(^3\).
Figure 25 Schematic of the geometry considered in the mathematical model of electron beam broadening (90)
The FORTRAN program to do these computations written for the VAX 11/780 computer is shown in Appendix C.
Chapter IV

MATERIALS AND EXPERIMENTAL PROCEDURES

4.1 Materials

The chemical compositions of the steels used in the study are given in Table 2. For the purpose of discussion, they can be conveniently divided into three groups, depending upon their carbon content. Steels in group A, B and C are respectively low, medium and high carbon type 304 stainless steels with varying nitrogen contents.

These steels were produced by laboratory melting and were forged and hot rolled to 4x100x250 mm sheet stock. All the steels were solution annealed at 1050°C for 15 minutes and then water quenched. The steels were then sensitized at 650°C. All heat treatments were carried out in an electric furnace under an argon atmosphere.

4.2 Experimental Procedures

The experimental procedures used in this investigation can be conveniently divided into two groups: the first used to study sensitization and the second used to study SCC.

4.2.1 Sensitization Studies

To study sensitization both electrochemical (EPR tests) and electron-optical (AEM investigation) techniques were used.
### Table 2 Chemical Composition of Materials

<table>
<thead>
<tr>
<th>Heat Number</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Cu</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-4</td>
<td>0.018</td>
<td>1.84</td>
<td>0.029</td>
<td>0.010</td>
<td>0.54</td>
<td>10.25</td>
<td>19.35</td>
<td>-</td>
<td>-</td>
<td>0.046</td>
</tr>
<tr>
<td>A-20</td>
<td>0.016</td>
<td>1.77</td>
<td>0.029</td>
<td>0.011</td>
<td>0.57</td>
<td>10.23</td>
<td>19.14</td>
<td>-</td>
<td>-</td>
<td>0.210</td>
</tr>
<tr>
<td>B-3</td>
<td>0.050</td>
<td>1.86</td>
<td>0.005</td>
<td>0.004</td>
<td>0.44</td>
<td>8.48</td>
<td>18.68</td>
<td>0.07</td>
<td>0.14</td>
<td>0.029</td>
</tr>
<tr>
<td>B-4</td>
<td>0.053</td>
<td>1.77</td>
<td>0.031</td>
<td>0.008</td>
<td>0.41</td>
<td>8.49</td>
<td>19.27</td>
<td>0.36</td>
<td>0.16</td>
<td>0.040</td>
</tr>
<tr>
<td>B-8</td>
<td>0.052</td>
<td>1.70</td>
<td>0.005</td>
<td>0.004</td>
<td>0.42</td>
<td>8.56</td>
<td>18.79</td>
<td>0.01</td>
<td>0.16</td>
<td>0.082</td>
</tr>
<tr>
<td>B-10</td>
<td>0.044</td>
<td>1.77</td>
<td>0.034</td>
<td>0.007</td>
<td>0.46</td>
<td>8.59</td>
<td>18.87</td>
<td>0.36</td>
<td>0.16</td>
<td>0.100</td>
</tr>
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<td>B-16A</td>
<td>0.053</td>
<td>1.70</td>
<td>0.005</td>
<td>0.005</td>
<td>0.40</td>
<td>8.53</td>
<td>18.92</td>
<td>0.01</td>
<td>0.14</td>
<td>0.160</td>
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<tr>
<td>B-16</td>
<td>0.043</td>
<td>1.78</td>
<td>0.028</td>
<td>0.008</td>
<td>0.41</td>
<td>8.63</td>
<td>18.80</td>
<td>0.38</td>
<td>0.16</td>
<td>0.160</td>
</tr>
<tr>
<td>B-24</td>
<td>0.046</td>
<td>1.88</td>
<td>0.005</td>
<td>0.004</td>
<td>0.48</td>
<td>8.62</td>
<td>18.91</td>
<td>0.01</td>
<td>0.17</td>
<td>0.240</td>
</tr>
<tr>
<td>B-25</td>
<td>0.046</td>
<td>1.37</td>
<td>0.030</td>
<td>0.008</td>
<td>0.40</td>
<td>8.89</td>
<td>18.90</td>
<td>0.38</td>
<td>0.17</td>
<td>0.250</td>
</tr>
<tr>
<td>C-4</td>
<td>0.076</td>
<td>1.88</td>
<td>0.031</td>
<td>0.010</td>
<td>0.55</td>
<td>9.94</td>
<td>19.35</td>
<td>-</td>
<td>-</td>
<td>0.039</td>
</tr>
<tr>
<td>C-20</td>
<td>0.070</td>
<td>1.73</td>
<td>0.029</td>
<td>0.012</td>
<td>0.56</td>
<td>10.12</td>
<td>19.20</td>
<td>-</td>
<td>-</td>
<td>0.200</td>
</tr>
</tbody>
</table>
4.2.1.1  **EPR Tests**

EPR tests were used to obtain the DOS and TTS diagrams. To study the effect of nitrogen on sensitization, solution annealed specimens were heated for up to 170 hours at various temperatures within the normal sensitization range (500-850°C) for austenitic stainless steels before water quenching. They were then polished to a 600 grit before testing. The susceptibility to intergranular corrosion of AISI 304 SS containing nitrogen was determined using the double loop version of the EPR test (141, 152). In the EPR test an anodic polarization curve in deaerated 0.5M H_2SO_4 + 0.01M KSCN solution at 30°C is obtained. The potential is first scanned in the anodic direction, starting from the corrosion potential, then held at 200 mV (vs SCE) for 2 minutes, and finally scanned in the reverse direction, as shown schematically in Figure 26. The voltage scan rate was 100mV/min. The activation ratio Ra, which is the parameter used to express the DOS of the steel, is the ratio of the maximum activation current to the critical passivation current.

4.2.1.2  **AEM Investigation**

AEM was used to obtain $X_{Cr}^i$ and the chromium concentration profiles across the grain boundaries. The experimental procedures involved have been described in detail elsewhere (246). The purpose of this investigation was mainly to compare its results with the predictions of the theoretical models of sensitization described in the previous chapter, and correlate its results to the SCC studies.
Figure 26 Definition of the activation ratio, $R_a$, which is the parameter used to express the DOS in the EPR test.
4.2.2 SCC Studies

To study susceptibility to SCC, both electrochemical and mechanical tests were carried out under controlled electrochemical and mechanical conditions in simulated BWR environments. Electron-optical examination of the fracture surface and dislocation structure were then performed. Electrochemical tests were used to study the anodic polarization behavior, which would help predict or explain occurrence of SCC. SSRTs were used to study the SCC susceptibility in both deareated 0.01M Na_2SO_4 and 0.01M NaCl at 250°C at various applied potentials and strain rates. SEM was used to examine the fracture and side surfaces, to determine the mode of failure and occurrence of pitting and secondary cracks. TEM was used to examine the dislocation structures obtained when these steels were deformed.

4.2.2.1 Anodic Polarization Tests

Flat specimens of dimensions 0.75 x 0.25 x 0.06" were used. They were polished to a 600 grit finish, rinsed with water and finally degreased with acetone before testing. The solution annealed specimens were sensitized at 650°C. Potentiodynamic polarization curves were measured for both solution annealed and sensitized steels, within the potential range -0.8 to 0.8 V_H, at a scan rate of 25 mV per minute in:

1) deareated 0.01M Na_2SO_4 (for samples sensitized for 2 hours at 650°C) and

2) deareated 0.01M NaCl (for samples sensitized for 50 hours at 650°C);

at 250°C using a PAR model 350 corrosion measurement system.
The high temperature/high pressure recirculating loop in which two titanium autoclaves were employed to test two specimens simultaneously is shown schematically in Figure 27. The loop consists of conditioning and storage tanks, a high pressure diaphragm pump, a preheater, two four liter titanium autoclaves connected in parallel and a heat exchanger, to recover heat from the outlet solution before discharge into the conditioning and storage tanks after passing through a cooler and a pressure control valve. All piping for the hot sections is made of titanium, whereas the remaining piping and the tanks are constructed of AISI 316 SS. The internal arrangement of the autoclave for anodic polarization tests is shown in Figure 28. It consists of the working electrode (specimen), the platinum counter electrode and an external reference electrode (in this case a silver/silver chloride/0.1N KCl electrode (247), the exploded view of which is shown in Figure 29. Potential values were converted to the conventional standard scale by using appropriate calibration data (247).

After the specimen was mounted inside the autoclave, high purity water contained in the conditioning and storage tanks was purged for about 12 hours with prepurified argon, to obtain a dissolved oxygen content of < 10 ppb. The high pressure pump was then activated, and the pressure was set at about 700 psi via the back pressure regulator. These parameters resulted in a fluid flow rate of about 0.6 liters/hour through each autoclave, and the temperature of the system was raised to 250°C. The potential was then measured and recorded. After approximately 4 hours a constant potential was attained. Now the polarization curves were measured. The oxygen content, the conductivity and the pH of the
Figure 27 Diagram of the high temperature/high pressure recirculating loop
Figure 28 Internal arrangement of the autoclave for anodic polarization tests
Figure 29 Exploded view of the external pressure-balanced reference electrode
inlet and outlet water were monitored before and after the test by sampling the solution. The oxygen content was determined by using a colorimetric technique. CHEMETS capsules for oxygen concentration ranges of 0-100 ppb were employed. The Beckman dissolved oxygen analyzer incorporated into the system did not perform satisfactorily, and therefore it was not employed. The conductivity was determined by using a conductivity bridge (Industrial Instruments, Model RC1682J). The conductivity of the inlet solution was maintained less than 0.3 μS/cm during the test. The pH was measured by using a pH meter (Corning Scientific Instruments, Model 5). The room temperature pH of the inlet solution was always within the range of 6.5 to 7.5 during the tests, which is a neutral solution.

4.2.2.2 SSRTs

Flat specimens of dimensions shown in Figure 30 were used. They were polished to a 600 grit finish, rinsed with water and finally degreased with acetone before testing. The solution annealed specimens were sensitized at 650°C. SSRTs were conducted under the following conditions:

1) Both solution annealed specimens and specimens sensitized for 2 hours at 650°C; tested in deaerated 0.01M Na₂SO₄ at 250°C, at a strain rate of 2 x 10⁻⁶ per second and at an applied potential of 0 Vₜ (since previous studies (23) have indicated that AISI 304 SS is most susceptible to IGSCC in this environment at a potential near 0 Vₜ). Tests were also carried out in an inert argon environment at 250°C, at a strain rate of 2 x 10⁻⁶ per
Figure 30  Design of the specimen used for the SSRTs
second. These tests were performed to study the effect of nitrogen and carbon on SCC susceptibility.

2) Specimens sensitized for 50 hours at 650°C; tested in deareated 0.01M NaCl at 250°C, at a strain rate of $2 \times 10^{-6}$ per second, at various applied potentials in the range $-0.4 \ V_H$ to $0.1 \ V_H$ and also under open circuit conditions. Tests were also carried out in an inert argon environment at 250°C, at a strain rate of $2 \times 10^{-6}$ per second. These tests were performed to study the effect of potential on SCC susceptibility.

3) Specimens sensitized for 50 hours at 650°C; tested in deareated 0.01M NaCl at 250°C, at an applied potential of $0 \ V_H$ and at various strain rates of $5 \times 10^{-7}$ to $1 \times 10^{-4}$ per second. These tests were performed to investigate which mechanism of SCC is operative.

The same high temperature/high pressure recirculating loop used for the polarization tests was used for the SSRTs. Specimens were electrically isolated from the titanium clevis attached to the pull rods by PTFE sheets. Pins were made of Zr-2.5 Nb alloy, and were coated with an insulating ZrO$_2$ film to avoid any electrical contact between the specimen and the autoclave. The internal arrangement of the autoclave for the SSRTs is shown in Figure 31. The temperature and pressure of the system is raised in the same manner described earlier for the polarization tests. After a constant corrosion potential was attained, an anodic potential was applied, and after approximately 12 hours a constant current was reached. The specimen was then strained at a nominal strain rate of $2 \times 10^{-6}$/s. Before straining, an initial load of
Figure 31  Internal arrangement of the autoclave for the SSRTs
about 50 lbs was applied. Bubbling of argon was continued throughout the test. The load and current were continuously recorded during the test. The oxygen content, the conductivity, and the pH of the inlet and outlet water, were monitored during the test by sampling the solution every 12 hours in the same manner described earlier. Their values were kept at the same levels as mentioned earlier.

After failure in the SSRTs the specimens were removed from the autoclave, sectioned, ultrasonically cleaned in acetone, and examined using a SEM; to characterize the fracture morphology and to examine the side surface for occurrence of pitting and secondary cracks.

TEM was used to examine the dislocation structures obtained when these steels were deformed. The experimental procedures involved in it have been described in detailed elsewhere (248).
Results and Analysis

This chapter is divided into two major sections: 5.1 deals with the sensitization studies and 5.2 with the SCC studies.

5.1 Sensitization Studies

This section is divided into five subsections to present the results and analysis of the: EPR tests in 5.1.1, thermodynamic modeling of sensitization in 5.1.2, AEM investigation in 5.1.3, kinetic modeling of sensitization in 5.1.4 and mathematical modeling of electron beam broadening in 5.1.5.

5.11 EPR Tests

Figures 32 - 35 show the Ra values obtained from the EPR tests, which indicate the DOS as a function of the sensitizing time at each temperature. For heat treatment temperatures of 550, 650, and 750°C, Ra was found to increase with increasing time in all cases. This effect is most pronounced at 650°C. No increase in Ra with heating time was observed at 850°C. This indicates that the upper temperature limit for sensitization of these steels lies between 750°C and 850°C.

On the basis of these results, TTS diagrams were constructed by plotting points having equivalent Ra values, for each steel, as a
Figure 32 $R_a$ (=DOS) as a function of sensitizing time at 550°C

Figure 33 $R_a$ (=DOS) as a function of sensitizing time at 650°C
Figure 34  $R_a$ (=DOS) as a function of sensitizing time at 750°C

Figure 35  $R_a$ (=DOS) as a function of sensitizing time at 850°C
function of time and temperature. Figures 36 and 37 show the TTS diagrams obtained for all the steels. For the B series steels (Figure 36), nitrogen additions up to 0.16 wt% have the effect of retarding sensitization; that is, the time required to achieve a given DOS increases with increasing nitrogen content. But the steel containing 0.25 wt% nitrogen was less resistant to sensitization because the TTS diagrams are shifted back to shorter times. It is clearly seen that for a fixed nitrogen level of 0.04 wt.%, carbon is detrimental to sensitization, since the TTS diagrams are shifted to shorter times with increasing carbon content, as shown in Figure 37.

5.1.2 Thermodynamic Modeling of Sensitization

Based on the thermodynamic model presented in section 3.1, the time, t, for sensitization to start at the temperatures of interest, 500-700°C, was calculated for a given steel composition with and without nitrogen additions. The TTS diagrams calculated for each steel with and without nitrogen, are compared with the experimental TTS diagrams obtained using the EPR tests for the same steel with nitrogen in Figures 38 - 41. To make this comparison, the calculated time, t, necessary to form a depleted zone of width 200Å, is compared with the experimentally determined time for a DOS of 5% at different sensitization temperatures. Such a comparison seems justified, since the stainless steel is sensitive to intergranular corrosion only when there is a chromium depleted zone of less than about 13 at % Cr and of a width larger than about 200Å (46). The calculations are for chromium diffusion limited growth and are valid for the low temperature portion
Figure 36 TTS diagrams for B series steels showing the effect of nitrogen on sensitization.
Figure 37 TTS diagrams for the steel with 0.04 wt.% nitrogen showing the effect of carbon on sensitization
Figure 38 Comparison between experimental TTS diagram of steel B-4 and calculated TTS diagrams for steel B-4 and steel B-4 without nitrogen

Figure 39 Comparison between experimental TTS diagram of steel B-10 and calculated TTS diagrams for steel B-10 and steel B-10 without nitrogen
Figure 40 Comparison between experimental TTS diagram of steel B-16 and calculated TTS diagrams for steel B-16 and steel B-16 without nitrogen.

Figure 41 Comparison between experimental TTS diagram of steel B-25 and calculated TTS diagrams for steel B-25 and steel B-25 without nitrogen.
of the TTS curve. At higher temperatures carbide nucleation is important and the theoretical model is not applicable.

Figures 38 - 41 illustrate that nitrogen additions up to 0.16 wt.% shift the TTS diagrams to increasing times and sensitization kinetics are retarded. At 0.25 wt% nitrogen the TTS diagram is shifted back to shorter times and sensitization kinetics are not retarded. The reason for the latter result is the greater amount of chromium carbides precipitating discontinuously, both by the Tu-Turnbull (249) and Fournelle-Clark (250) mechanism, resulting in grain boundary migration and wider chromium depleted regions (246). This aspect is analyzed in more detail in subsection 5.1.3 on AEM investigation. For the stainless steels containing up to 0.16 wt.% nitrogen, most of the chromium carbides were precipitated continuously at the grain boundaries (246), and their growth is controlled by diffusion of chromium from the austenite matrix to the grain boundaries, so for these steels the thermodynamic model presented in Chapter 3 is valid. The reason for the retardation of sensitization kinetics with nitrogen additions from 0.04 up to 0.16 wt.%, is due to the increase in the chromium content at the carbide-austenite interface, as shown in Figure 42. This is seen from:

1. Calculations based on the sensitization time from the EPR test results using equation [40]; $X_{Cr}^{i}$ increases from 8.6 to 11.0 wt.%, as nitrogen is increased from 0.04 to 0.16 wt.%,
2. Calculations based on the thermodynamic model; $X_{Cr}^{i}$ increases from 7.9 to 9.4 wt.%, as nitrogen is increased from 0.04 to 0.16 wt.%.

The discrepancy in the values of the chromium content at the
Figure 42 Chromium content at the carbide-austenite interface as a function of nitrogen content in B series steel.
carbide-austenite interface, obtained by the two methods, is due to various assumptions made in the development of the thermodynamic model, and in comparing it to the EPR results.

The effect of carbon on the TTS diagrams obtained by the EPR tests was shown in Figure 37. The same deleterious effect is observed when the effect of carbon on the TTS diagrams, obtained using the thermodynamic model, is plotted, as shown in Figure 43. It illustrates that as carbon is increased from 0.02 to 0.07 wt.%, for a steel containing 0.04 wt.% nitrogen, the TTS diagrams are shifted to shorter times and sensitization is promoted. The reason for this deleterious effect with carbon additions is due to the decrease in the chromium content at the carbide-austenite interface, as shown in Figure 44. This is seen from:

1. Calculations based on the sensitization time from the EPR test results using equation [40]; $X^1_{Cr}$ decreases from 11.2 to 8.6 wt.%, as carbon is increased from 0.02 to 0.07 wt.%
2. Calculations based on the thermodynamic model; $X^1_{Cr}$ decreases from 10.7 to 7.2 wt.%, as carbon is increased from 0.02 to 0.07 wt.%

The reasons for the discrepancy in the values of the chromium content at the carbide-austenite interface, obtained by the two methods, is the same as those for the case of nitrogen shown in Figure 42.

5.1.3 AEM Investigation

In the previous subsection, based on computations using the thermodynamic model and EPR results, it was shown that $X^1_{Cr}$ increases with nitrogen additions, and $X^1_{Cr}$ decreases with carbon additions. X-ray
Figure 43 Calculated TTS diagrams for the steel with 0.04 wt.% nitrogen showing the effect of carbon on sensitization.
Figure 44 Chromium content at the carbide-austenite interface as a function of carbon content in the steel with 0.04 wt.% nitrogen
microanalysis carried out in the AEM also indicates this; $X_{Cr}^I$ increases from 10.9 to 12.1 wt.%, with nitrogen additions from 0.04 up to 0.16 wt.% as shown in Figure 42; and $X_{Cr}^I$ decreases from 13.3 to 10.2 wt.%, with carbon additions from 0.02 to 0.07 wt.%, as shown in Figure 44. The discrepancy in the values of $X_{Cr}^I$ obtained using the AEM and the computations is due to the effect of electron beam broadening in the AEM samples, which is analyzed in subsection 5.1.5. The values of $X_{Cr}^I$ were taken as grain boundary chromium concentration, because of the rapid grain boundary diffusivity of chromium and the absence of a chromium concentration gradient between $\text{Cr}_2\text{C}_6$ precipitates along the grain boundary (246). The chromium concentration profiles across the grain boundary, at which $\text{Cr}_2\text{C}_6$ is precipitated by volume diffusion controlled growth, are shown in Figures 45 and 46. For the B series steels (Figure 45) it is seen that nitrogen additions up to 0.16 wt.% increase the grain boundary chromium concentration from 10.9 to 12.1 wt.%. It is not possible to quantify the width of the chromium concentration profiles in Figure 45, because of the scatter in the experimental data. The effect of nitrogen on the width of the chromium concentration profiles is analyzed in the next subsection on kinetic modeling of sensitization. In Figure 46 it is clearly seen that for a fixed nitrogen level of 0.04 wt.%; carbon additions from 0.02 to 0.07 wt.%, decrease the grain boundary chromium concentration from 13.3 to 10.2 wt.%. Again it is not possible to quantify the width of the chromium concentration profiles in Figure 46, because of the scatter in the experimental data. The effect of carbon on the width of the chromium concentration profiles is analyzed in the next subsection on kinetic modeling of sensitization.
Figure 45 Chromium concentration profiles across the grain boundaries as a function of nitrogen for B the series steels
Figure 46 Chromium concentration profiles across the grain boundaries as a function of carbon for the steels with 0.04 wt.% nitrogen.
It was stated earlier that for the B series steel at 0.25 wt.% nitrogen, the TTS diagram is shifted back to shorter times and sensitization is not retarded; the reason for this was the greater amount of Cr$_{23}$C$_6$ precipitating discontinuously, resulting in grain boundary migration and wider chromium depleted regions. Evidence for this is seen in Figure 47, which shows the asymmetric chromium concentration profile across a migrating boundary (at which Cr$_{23}$C$_6$ has precipitated discontinuously), which leaves behind a wide chromium depleted region.

5.1.4 Kinetic Modeling of Sensitization

Based on the kinetic model presented in section 3.2, the chromium concentration profile across the grain boundary at which Cr$_{23}$C$_6$ is precipitated by volume diffusion controlled growth was calculated using equation [56], and is shown in Figure 48. The values for $C_i$ and $D$ used were those obtained experimentally using the AEM; in this manner the effect of nitrogen was incorporated into the kinetic model. The values for $C_m$ can be obtained from the steel composition and were taken as 18.9 wt.% for the computations. The carbide radius ($r_i$) was taken as 0.1 μm for the computations. The values of all these input parameters into the model are shown in Table 3. Figure 48 shows that, as long as Cr$_{23}$C$_6$ is precipitated by volume diffusion controlled growth, the width of the chromium concentration profile decreases with increasing nitrogen. This result again explains why nitrogen additions retard sensitization in the EPR test, which is sensitive to both the width of chromium depletion and the minimum chromium concentration at the grain boundary. However as it
Figure 47  Asymmetric chromium concentration profile across a migrating boundary which leaves behind a wide chromium depleted region in B-25 steel.
Figure 48 Calculated chromium concentration profiles across the grain boundaries as a function of nitrogen for the B series steels.
was pointed out earlier, at 0.25 wt.% nitrogen, $\text{Cr}_2\text{C}_6$ is precipitated discontinuously, leading to wide chromium depletion behind migrating grain boundaries and sensitization is not retarded.

Table 3

Values of Input Parameters into the Kinetic Model; to Study the Effect of Nitrogen on Sensitization.

<table>
<thead>
<tr>
<th>Steel</th>
<th>$C_i$ (wt.%)</th>
<th>$D$ (cm²/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-4</td>
<td>10.9</td>
<td>$3.0 \times 10^{-16}$</td>
</tr>
<tr>
<td>B-10</td>
<td>11.4</td>
<td>$1.8 \times 10^{-16}$</td>
</tr>
<tr>
<td>B-16</td>
<td>11.8</td>
<td>$1.1 \times 10^{-16}$</td>
</tr>
<tr>
<td>B-25</td>
<td>12.1</td>
<td>$0.8 \times 10^{-16}$</td>
</tr>
</tbody>
</table>

$C_m = 18.9$ wt.%

$r_f = 0.1$ μm

The effect of carbon on the width of the chromium concentration profiles was calculated in a similar manner and is shown in Figure 49. The values of input parameters into the kinetic model are shown in Table 4. Figure 49 shows that the width of the chromium concentration profile increases with increasing carbon, which again explains why carbon promotes sensitization.
Figure 49 Calculated chromium concentration profiles across the grain boundaries as a function of carbon for the steel with 0.04 wt.% nitrogen.
Table 4
Values of Input Parameters into the Kinetic Model; to Study the Effect of Carbon on Sensitization.

<table>
<thead>
<tr>
<th>Steel</th>
<th>( C_i ) (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-4</td>
<td>13.3</td>
</tr>
<tr>
<td>B-4</td>
<td>10.9</td>
</tr>
<tr>
<td>C-4</td>
<td>10.2</td>
</tr>
</tbody>
</table>

\( C_m = 19.4 \text{ wt.\%} \)
\( r_i = 0.1 \mu \text{m} \)
\( D = 8.6 \times 10^{-16} \text{ cm}^2/\text{sec} \).

The chromium concentration profile across the grain boundary, calculated using the kinetic model and obtained experimentally using the AEM, is shown in Figures 50 and 51 for A-4 steel. The value of \( C_m \) is obtained from the steel composition, which is 19.35 wt.\%. The value of \( r_i \) was taken as 0.1 \( \mu \)m and \( D \) was taken as \( 8.6 \times 10^{-16} \text{ cm}^2/\text{sec} \) (49). In Figure 50, the value of \( C_i \) was taken as 10.7 wt.\%, which is that calculated using the thermodynamic model. It is clearly seen that the calculated and experimental profiles do not match, especially at the grain boundary. The experimental value shows a high chromium concentration at the grain boundary, which is due to higher counts during the X-ray microanalysis in the AEM because of electron beam broadening. In Figure 51 the value of \( C_i \) was taken as 13.3 wt.\%, to match the experimental AEM value; now the agreement between the
Figure 50 Comparison between the calculated and experimental chromium concentration profiles across grain boundaries in sensitized A-4 steel when $C_i=10.7$ wt.%
Figure 51  Comparison between the calculated and experimental chromium concentration profiles across grain boundaries in sensitized A-4 steel when $C_i = 13.3$ wt.\%
calculated and experimental profiles is reasonable. The agreement between the two can be further improved by considering the effect of electron beam broadening which is considered next.

5.1.5 Mathematical Modeling of Electron Beam Broadening

Based on the mathematical model presented in section 3.3, the chromium concentration profile across the grain boundary, calculated using equation [59] for A-4 steel, is shown in Figure 52(a). The equilibrium value of chromium of 10.65 wt.%, calculated using the thermodynamic model was used for calculating the profile in Figure 52(a). This calculated profile is then described as a Gaussian curve, with the same height and half width, which is shown in Figure 52(b); in order to compare it with the experimental profile, shown in Figure 52(c), that would be obtained using the AEM when the mathematical model is applied. The incident electron probe size was taken as 10 nm and the foil thickness was taken as 200 nm in these calculations. Now the agreement between the calculated and experimentally determined chromium concentration profiles is seen to be better.

5.2 SCC Studies

This section is subdivided into two, to present the results and analysis of SCC studies in high temperature sulphate solutions in 5.2.1, and SCC studies in high temperature chloride solutions in 5.2.2. Sulphate and chloride ions are present in the BWR environment due to thermal and/or radiolytic decomposition of cationic resins.
Figure 52(a) Calculated chromium concentration profile across grain boundaries in sensitized A4 steel
(b) Gaussian fit to the calculated chromium concentration profile across grain boundaries in sensitized A4 steel
(c) Experimental chromium concentration profile that would be obtained using the AEM when the mathematical model is applied for A4 steel
5.2.1 SCC Studies in Sulphate Solutions

This section is divided into four subsections to present the results and analysis of the: anodic polarization behavior in 5.2.1.1, effect of nitrogen on SCC susceptibility in 5.2.1.2, effect of nitrogen on fracture morphology in 5.2.1.3, and effect of nitrogen on dislocation structure in 5.2.1.4.

5.2.1.1 Anodic Polarization Behavior

Polarization curves measured for solution annealed and sensitized B series steels containing different levels of nitrogen are shown in Figures 53 - 56. The common features of these polarization curves are:

(a) a corrosion potential of about -650 mV$_H$,
(b) the presence of an active/passive peak, and
(c) a transpassive peak

(labeled a, b and c respectively in Figures 53 - 56). The shape of the polarization curves for solution annealed and sensitized stainless steels are similar, but the latter show slightly higher current densities. This observation is consistent with the results of Indig and Vermilyea (236), and Kushiya et. al. (237). In general, it was not possible to observe any influence of nitrogen on the anodic polarization behavior of these stainless steels, nor were any effects seen on the polarization curves which would explain or predict the observed SCC performance which is presented next.

5.2.1.2 Effect of Nitrogen on SCC Susceptibility

It is necessary to normalize the SSRT results obtained in the
Figure 53  Polarization curves for solution annealed and sensitized 84 in 0.01M Na₂SO₄ at 250°C
Figure 54  Polarization curves for solution annealed and sensitized B10 in 0.01M Na₂SO₄ at 250°C.
Figure 55  Polarization curves for solution annealed and sensitized B16 in 0.01M Na₂SO₄ at 250°C
Figure 56  
Polarization curves for solution annealed and sensitized B25 in 0.01M Na₂SO₄ at 250°C
corrosive environment with respect to those obtained in an inert argon environment; the results of which are shown in Figure 57, in which the maximum stress and elongation to fracture are plotted as a function of nitrogen and carbon content. It is seen that the maximum stress increases with both increasing carbon and nitrogen; but the elongation to failure remains constant with increasing carbon and nitrogen content.

The results of the SSRTs in sulphate solutions are shown in Figures 58 and 59, in which the nominal stress is plotted as a function of elongation for solution annealed and sensitized AISI 304 stainless steels with various carbon and nitrogen contents. The solution annealed stainless steels exhibit the highest values of elongation to failure, while in the sensitized stainless steels the composition has a significant effect on the elongation to failure and on the shape of the nominal stress versus elongation curves. The sensitized A steels show a high elongation to failure and a high SCC resistance. In the sensitized B series steels, the elongation to failure increases with nitrogen additions up to about 0.16 wt.%, which correlates with their improvement in SCC resistance. The increase in the elongation to failure obtained with nitrogen additions was accompanied by a change in the shape of the nominal stress versus elongation curves just after reaching the maximum stress. For the sensitized stainless steels that suffered SCC after the maximum nominal stress was reached the nominal stress decreased to very low value before the ductile failure of the remaining cross sectional area occurred. The sensitized C steels show a low elongation to failure and a low nominal stress at failure, as well as low SCC resistance.

The effect of nitrogen and carbon on susceptibility to SCC is shown
Figure 57 Maximum stress and elongation to failure as a function of nitrogen and carbon content.
Type 304 Stainless Steel (B-4 ~ B-25)
0.01 M Na₂SO₄, T=250°C, Deareated
\( \dot{\varepsilon} = 2 \times 10^{-6} \text{ sec}^{-1} \), \( E = 0 \text{ V}_{H} \)

Figure 58 Nominal stress as a function of elongation for solution annealed and sensitized B series steels
Type 304 Stainless Steel (A-4, A-20) (C-4, C-20)
0.01 M Na$_2$SO$_4$, T=250°C, Deareated
$\dot{\varepsilon} = 2 \times 10^6$ sec$^{-1}$, $E=0V_H$

Figure 59 Nominal stress as a function of elongation for solution annealed and sensitized A and C series steels
in Figures 60 and 61. Figure 60 shows a plot of the normalized elongation to failure (the ratio of elongation to failure in a corrosive solution to that observed in an inert argon environment) as a function of nitrogen for the B series steels. The normalized elongation to failure for the solution annealed B series steels is almost constant with nitrogen additions, but for the sensitized B steels it increases with nitrogen additions up to about 0.16 wt.%, making the steel less susceptible to SCC. The deleterious effect of carbon on SCC resistance is seen in Figure 61, in which the normalized elongation to failure is seen to decrease with carbon additions to sensitized stainless steels containing 0.04 and 0.20 wt.% nitrogen.

5.2.1.3 Effect of Nitrogen on Fracture Morphology

The effect of nitrogen on the fracture surface morphologies of the sensitized B steels is shown in Figure 62. These fracture surfaces consist of a coarse granular region, A, through which the crack has propagated either intergranularly and/or transgranularly, and a flat region, B, which is the final ductile failure due to mechanical overloading. Figure 63 shows that IGSCC occurs at 0.04 wt.% nitrogen, but TGSCC exists together with IGSCC at 0.25 wt.% nitrogen. Figure 64 shows the measured fractions of ductile and SCC fracture surface areas, as a function of nitrogen content, for the sensitized B steels; the susceptibility to IGSCC decreases with nitrogen additions up to about 0.16 wt.%, but TGSCC occurs at higher nitrogen additions.
Figure 60 Normalized elongation to failure as a function of nitrogen content for solution annealed and sensitized B series steels in sulphate solutions.
Type 304 Stainless Steel
Sensitized 2 hrs at 650°C
0.01M Na₂SO₄, T=250°C, Deoxygenated
\( \dot{\varepsilon} = 2 \times 10^{-6} \text{ sec}^{-1}, E = 0 \text{ V}_f \)

\[ \text{Normalized Elongation to Fracture} \quad \frac{\varepsilon_f}{\varepsilon_{f, \text{Argon}}} \]

Figure 61 Normalized elongation to failure as a function of carbon content for sensitized AISI 304 stainless steels in sulphate solutions
Figure 62  Effect of nitrogen on the fracture surface morphologies of sensitized B steels, region A is due to intergranular and/or transgranular failure and region B is due to ductile failure. a,b,c and d are the fracture surfaces of sensitized B4, B10, B16 and B25 steels respectively.
Figure 63  Transition in the mode of cracking of sensitized B steels with increasing nitrogen additions. a and b are the fracture surfaces of sensitized B4 and B25 steels respectively.
Figure 64 Area fraction of ductile and SCC fracture surface as a function of nitrogen content for sensitized B series steels.
5.2.1.4 **Effect of Nitrogen on Dislocation Structures**

SEM observations showed that a transition from IGSCC to TGSCC occurs with increasing nitrogen additions. TEM examination suggests that this may be due to the change in the dislocation structure (195), with increasing nitrogen additions, from a cellular to a planar array of mobile dislocations (Figure 65). This is thought to be due to a decrease in stacking fault energy of austenite as the nitrogen content increases (15, 196, 197).

5.2.2 **SCC Studies in Chloride Solutions**

This section is divided into five subsections, to present the results and analysis of the: anodic polarization behavior in 5.2.2.1, effect of potential on SCC susceptibility in 5.2.2.2, effect of potential on fracture morphology in 5.2.2.3, effect of strain rate on SCC susceptibility in 5.2.2.4, and effect of strain rate on fracture morphology in 5.2.2.5.

5.2.2.1 **Anodic Polarization Behavior**

Polarization curves obtained for all the steels in 0.01M NaCl at 250°C are shown in Figures 66 - 73. In these figures the solid lines represent the polarization curve for the solution annealed material and the dotted lines represent the polarization curve for the steels sensitized at 650°C for 50 hours. The common features of these polarization curves are:

(a) a corrosion potential of about -550 mV$_H$,

(b) the existence of a passive region, and
Figure 65  Change in dislocation structure of sensitized B steels with increasing nitrogen additions. a and b are TEM micrographs of sensitized B-4 and B-25 steels respectively.
Figure 65
Figure 66 Polarization curves for solution annealed and sensitized A-4 in 0.01M NaCl at 250°C
Figure 67 Polarization curves for solution annealed and sensitized A-20 in 0.01M NaCl at 250°C
Figure 68  Polarization curves for solution annealed and sensitized B-3 in 0.01M NaCl at 250°C
Figure 69  Polarization curves for solution annealed and sensitized B-8 in 0.01M NaCl at 250°C
Figure 70. Polarization curves for solution annealed and sensitized B-16 in 0.01M NaCl at 250°C.
B-24
0.01 M NaCl, T=250°C
Deaerated, Scan Rate=25 mV/min

Figure 71  Polarization curves for solution annealed and sensitized B-24 in 0.01M NaCl at 250°C
Figure 72  Polarization curves for solution annealed and sensitized C-4 in 0.01M NaCl at 250°C
Figure 73 Polarization curves for solution annealed and sensitized C-20 in 0.01M NaCl at 250°C
The shape of the polarization curves for solution annealed and sensitized stainless steels are similar, but the later show slightly higher current densities. In general, it was not possible to observe any major influence of nitrogen on the anodic polarization behavior of the sensitized stainless steels. But for the sensitized B series steels nitrogen up to 0.16 wt.%, did decrease the passive current density, while nitrogen of 0.25 wt.% did not, as shown in Figure 74. Figure 75 shows a pitting scan, which shows that the breakdown of passivity in these steels is due to the onset of pitting corrosion.

5.2.2.2 Effect of Potential on SCC Susceptibility

In order to evaluate the susceptibility of the steels to SCC by SSRT, it was necessary to normalize the data for each material with respect to a standard test in an inert environment such as argon, air or oil under the same condition. For this purpose, the tensile properties of the stainless steels were determined using SSRTs in an argon atmosphere. The test temperature and the strain rate were the same as used for the subsequent SSRTs in the corrosive environment, i.e., $T = 250^\circ\text{C}$ and $\dot{\varepsilon} = 2\times10^{-6}$ sec$^{-1}$. The ultimate tensile strength and the elongation to fracture are plotted in Figure 76, as a function of nitrogen content of the steels, for a carbon level of 0.05 wt.%. The strength of the steels increased with increasing nitrogen content. On the other hand the elongation to fracture of each steel was nearly the same, irrespective of the nitrogen content.

The results of slow strain rate tests carried out at various
Figure 74 Effect of nitrogen on passive current density of sensitized B series steels in 0.01M NaCl at 250°C
Figure 75  Pitting scan for sensitized A-20 in 0.01M NaCl at 250°C
Type 304 Stainless Steel
(B-3 ~ B-24)
Solution Annealed 15 min.
at 1050°C

Figure 76 Maximum stress and elongation to failure as a function of nitrogen for the B series steels
applied potentials for the various steels are summarized in Table 5. The results of SSRTs performed at various applied potentials for all the steels are plotted in Figures 77 - 84 respectively. These figures show the nominal stress vs elongation curves that were obtained at different applied potentials. A pronounced effect of potential on the stress vs elongation curve was observed. At those potentials where SCC occurred the elongation to failure decreased compared to ductile failure. The decrease in the elongation to failure of these steels in the potential range -300 to 100 mV_H is clearly related to an increase in the susceptibility to SCC. The decrease in elongation to failure obtained in this potential range is accompanied by a change in the shape of the stress-elongation curves just after reaching the maximum stress, in comparison to the same portion of the curve at other potentials. After reaching the maximum, the stress decreased to very low values, just before the sudden drop produced by the ductile failure of the remaining cross sectional area. In all of these experiments, no change in the current density was observed during the slow strain rate tests, except in some tests in which a slight increase in current accompanied the final decrease in stress.
Table 5

Results of SSRTs for sensitized AISI 304 SS with varying carbon and nitrogen levels, in 0.01M NaCl solution at 250°C, under applied potential and open circuit conditions.

<table>
<thead>
<tr>
<th>Steel (mV SHE)</th>
<th>Elongation to failure (%)</th>
<th>Time to failure (hours)</th>
<th>Maximum Stress (ksi)</th>
<th>Fracture Morphology</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-4 0.0</td>
<td>49.68</td>
<td>69.00</td>
<td>54.49</td>
<td>D</td>
<td></td>
</tr>
<tr>
<td>A-4 -200</td>
<td>49.68</td>
<td>69.00</td>
<td>57.13</td>
<td>D</td>
<td></td>
</tr>
<tr>
<td>A-4 -100</td>
<td>46.80</td>
<td>65.00</td>
<td>57.13</td>
<td>D</td>
<td></td>
</tr>
<tr>
<td>A-4 -50</td>
<td>45.72</td>
<td>63.50</td>
<td>62.75</td>
<td>D</td>
<td></td>
</tr>
<tr>
<td>A-4 0</td>
<td>27.18</td>
<td>37.75</td>
<td>52.51</td>
<td>D+T+P</td>
<td></td>
</tr>
<tr>
<td>A-4 100</td>
<td>18.72</td>
<td>26.00</td>
<td>37.65</td>
<td>D+T+P</td>
<td></td>
</tr>
<tr>
<td>A-20 0.0</td>
<td>51.12</td>
<td>71.00</td>
<td>77.61</td>
<td>D</td>
<td></td>
</tr>
<tr>
<td>A-20 -200</td>
<td>42.48</td>
<td>59.00</td>
<td>75.30</td>
<td>D</td>
<td></td>
</tr>
<tr>
<td>A-20 -100</td>
<td>18.54</td>
<td>25.75</td>
<td>47.56</td>
<td>D+I</td>
<td></td>
</tr>
<tr>
<td>A-20 -60</td>
<td>7.20</td>
<td>7.00</td>
<td>22.13</td>
<td>D+I Secondary Cracks</td>
<td></td>
</tr>
<tr>
<td>A-20 0</td>
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<td>7.00</td>
<td>22.13</td>
<td>D+I</td>
<td></td>
</tr>
<tr>
<td>A-20 100</td>
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<td>30.50</td>
<td>48.88</td>
<td>D+I+T+P</td>
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</tr>
<tr>
<td>C-4 0.0</td>
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<td>71.00</td>
<td>71.00</td>
<td>D</td>
<td></td>
</tr>
<tr>
<td>C-4 -400</td>
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<td>63.25</td>
<td>66.10</td>
<td>D</td>
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<td>C-4 -200</td>
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<td>14.86</td>
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<td>C-20 0.0</td>
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<td>52.50</td>
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<td>27.41</td>
<td>D+I</td>
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<td>Steel (mV SHE)</td>
<td>E (%)</td>
<td>Time to Failure (hours)</td>
<td>Maximum Stress (ksi)</td>
<td>Failure Morphology</td>
<td>Remarks</td>
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<td>-------</td>
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<td>26.42</td>
<td>D+I</td>
<td>Secondary Cracks</td>
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<tr>
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<td>20.50</td>
<td>48.22</td>
<td>D+I+T+P</td>
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<td>60.00</td>
<td>83.55</td>
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<td>57.00</td>
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<tr>
<td>B-3 -300</td>
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<td>20.00</td>
<td>32.03</td>
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<tr>
<td>B-3 -200</td>
<td>5.40</td>
<td>7.50</td>
<td>22.79</td>
<td>D+I</td>
<td></td>
</tr>
<tr>
<td>B-3 -100</td>
<td>3.24</td>
<td>4.50</td>
<td>16.51</td>
<td>D+I</td>
<td>Secondary Cracks</td>
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<tr>
<td>B-3 100</td>
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<td>8.25</td>
<td>20.48</td>
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<td>B-8 O.C</td>
<td>36.72</td>
<td>51.00</td>
<td>70.67</td>
<td>D</td>
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<tr>
<td>B-8 -400</td>
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<td>57.00</td>
<td>64.40</td>
<td>D</td>
<td></td>
</tr>
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<td>B-8 -300</td>
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<td>29.06</td>
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<td>3.00</td>
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<tr>
<td>B-8 0</td>
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<td>10.00</td>
<td>23.78</td>
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<tr>
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<td>75.63</td>
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<tr>
<td>B-16 -300</td>
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<td>D+I</td>
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<tr>
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<td>23.78</td>
<td>D+I+P</td>
<td></td>
</tr>
<tr>
<td>B-24 O.C</td>
<td>44.64</td>
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<td>87.52</td>
<td>D</td>
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<tr>
<td>B-24 -400</td>
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<td>77.94</td>
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<td>38.31</td>
<td>D+I</td>
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<tr>
<td>B-24 -200</td>
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<td>8.00</td>
<td>30.05</td>
<td>D+I</td>
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<tr>
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<td>5.25</td>
<td>19.82</td>
<td>D+I+P</td>
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Figure 77 Nominal stress vs. elongation for A-4 steel in 0.01M NaCl at 250°C and $\dot{\varepsilon} = 2 \times 10^{-6} \text{ sec}^{-1}$ at various applied potentials.
Figure 78 Nominal stress vs. elongation for A-20 steel in 0.01M NaCl at 250°C and \( \dot{\varepsilon} = 2 \times 10^{-6} \text{sec}^{-1} \) applied potentials.
Figure 79 Nominal stress vs. elongation for B-3 steel in 0.01M NaCl at 250°C and \( \dot{\varepsilon} = 2 \times 10^{-6} \text{ sec}^{-1} \).
Figure 80 Nominal stress vs. elongation for B-8 steel in 0.01M NaCl at 250°C and \( \dot{\varepsilon} = 2 \times 10^{-6} \text{sec}^{-1} \) at various applied potentials.
Figure 81 Nominal stress vs. elongation for B-16 steel in 0.01M NaCl at 250°C and $\dot{\varepsilon} = 2 \times 10^{-6}$ sec$^{-1}$ per second at various applied potentials.
Figure 82 Nominal stress vs. elongation for B-24 steel in 0.01M NaCl at 250°C and $\dot{\varepsilon} = 2 \times 10^{-6}$ sec$^{-1}$ per second at various applied potentials.
Figure 83 Nominal stress vs. elongation for C-4 steel in 0.01M NaCl at 250°C and $\dot{\varepsilon} = 2 \times 10^{-6}$ sec$^{-1}$ at various applied potentials.
Figure 84 Nominal stress vs. elongation for C-20 steel in 0.01M NaCl at 250°C and $\dot{\varepsilon} = 2 \times 10^{-6}$ sec$^{-1}$ at various applied potentials.
In Table 5 O.C refers to the test under open circuit conditions, I refers to intergranular cracking, T refers to transgranular cracking, D refers to ductile failure, and P refers to pitting.

As stated above, the nominal stress vs. elongation curves give a clear indication of the effect of potential on the tendency towards SCC, and therefore the elongation to failure can be used as an adequate parameter to assess cracking susceptibility. For that reason, the ratio of the elongation to failure when SCC was observed to that corresponding to ductile failure in an argon atmosphere at 250°C, is plotted as a function of potential in Figures 85 - 87 for the various steels. It is seen from these figures that SCC occurs above a certain critical potential ($E_{SCC}$), which varies between $-0.3 \ V_H$ to $0 \ V_H$, and is dependent on the carbon and nitrogen content of the stainless steel. Figure 85 shows that nitrogen additions up to 0.16 wt.% increase $E_{SCC}$, while a nitrogen level of 0.25 wt.% does not. Figures 86 and 87 show that, $E_{SCC}$ decreases with increasing carbon, at fixed nitrogen levels of 0.04 and 0.20 wt.% respectively.

The effect of nitrogen on SCC susceptibility in chloride solution at $-0.3 \ V_H$ is shown in Figure 88. It is seen that nitrogen additions up to 0.16 wt.% increase the SCC resistance, while a nitrogen addition of 0.24 wt.% decreases it. The effect of carbon on SCC resistance in chloride solution at $-0.05 \ V_H$ is shown in Figure 89. It is seen that carbon additions to a 0.04 wt.% nitrogen steel decreases the SCC resistance.
Figure 85 Normalized elongation to failure vs. potential for B series steels tested in 0.01M NaCl at 250°C and $\dot{\varepsilon} = 2 \times 10^{-6}$ s$^{-1}$; showing the effect of nitrogen on IGSCC.
Figure 86 Normalized elongation to failure vs. potential for the steel with 0.04 wt. % nitrogen tested in 0.01M NaCl at 250°C and $i = 2 \times 10^{-6}$ s$^{-1}$ showing the effect of carbon on $E_{IGSCC}$.
Figure 87 Normalized elongation to failure vs. potential for the steel with 0.20 wt.% nitrogen tested in 0.01M NaCl at 250°C and \( \dot{\varepsilon} = 2 \times 10^{-6} \text{s}^{-1} \), showing the effect of carbon on IGSCC.
Figure 88  Normalized elongation to failure vs. nitrogen content for sensitized B series steels in chloride solution at -0.3 $V_H$
Type 304 Stainless Steel
with $N = 0.04$ wt. %
0.01M NaCl, $T = 250^\circ C$, Dearated
$\dot{\epsilon} = 2 \times 10^{-6} \text{sec}^{-1}$, $E = -0.05 V_H$

Figure 89 Normalized elongation to failure vs. carbon content for sensitized steels with 0.04 wt.% nitrogen in chloride solution at $-0.05 \ V_H$
5.2.2.3 Effect of Potential on Fracture Morphology

SEM examination shows that the predominant fracture mode at potentials below $E_{\text{SCC}}$ was ductile; and at potentials above $E_{\text{SCC}}$ was IGSCC for all the compositions studied, with the exception of the A-4 stainless steel. TGSCC along with shallow pitting on the side surface was observed in this latter case, as well as for most other alloys at high potentials. These results are summarized in Table 5 and Figures 85 - 87, in which the predominant fracture morphology is shown. These results are substantiated and analyzed in detail, by presenting the SEM micrographs for all the steels studied.

For A-4 stainless steel at open circuit and $-0.05 \ V_H$, which are below $E_{\text{SCC}}$, ductile failure was observed; and at potentials of 0 and 0.1 $V_H$, which are above $E_{\text{SCC}}$, mainly TGSCC and small areas of ductile dimples in the fracture surface, and numerous broad and shallow pits were observed on the side surface which are related to the breakdown of passivity at high potentials. The ratio of TGSCC area to ductile area increased with increasing the potential from 0 to 0.1 $V_H$. These fractographs for A-4 stainless steel are shown in Figure 90.

For A-20 stainless steel at $-0.2 \ V_H$, which is below $E_{\text{SCC}}$, ductile failure was observed; and at potentials of $-0.1$ and $-0.06 \ V_H$ mainly IGSCC and small areas of ductile dimples were observed on the fracture surface. The ratio of IGSCC area to ductile area increased with increasing the potential from $-0.1$ to $-0.06 \ V_H$. At $-0.06 \ V_H$ secondary intergranular cracks were observed on the side surface. These cracks are deep and very different from the broad and shallow pits observed at a higher potentials of 0.1 $V_H$. At 0.1 $V_H$ the fracture mode was partly
Figure 90  SEM fractographs for A-4 stainless steel
a Ductile failure at open circuit.
b Ductile failure at -0.05 $V_H$.
c TGSSC at 0 $V_H$.
d Pitting at 0 $V_H$.
e TGSSC at 0.1 $V_H$.
f Pitting at 0.1 $V_H$. 
IGSCC and partly TGSCC, careful examination of the fracture surface shows that the intergranular and transgranular cracks initiated simultaneously on the surface of the sample and grew independently after starting at different places to give the final fracture. These fractographs for A-20 stainless steel are shown in Figure 91.

For B-3 stainless steel at -0.4 $V_H$, which is below $E_{SCC}$, ductile failure was observed; and at potentials of -0.3, -0.2, -0.1 and 0.1 $V_H$ mainly IGSCC was observed. At -0.1 $V_H$ secondary intergranular cracks were observed on the side surface. At the high potential of 0.1 $V_H$ no TGSCC was observed and the fracture mode was completely IGSCC. This was the case for all the B series steels. The reason for this is thought to be due to severe sensitization in these steels, which were obtained from Armco Incorporation, because of heat to heat differences which affect IGSCC behavior (22). But broad and shallow pits were observed on the side surface at the high potential of 0.1 $V_H$. These fractographs for B-3 stainless steel are shown in Figure 92.

For B-8 stainless steel at -0.4 $V_H$, which is below $E_{SCC}$, ductile failure was observed; at potentials of -0.3, -0.2, -0.1 and 0 $V_H$ mainly IGSCC was observed. At 0 $V_H$ broad and shallow pits were observed on the side surface. These micrographs for B-8 stainless steel are shown in Figure 93.

For B-16 stainless steel at -0.3 $V_H$, which is below $E_{SCC}$, ductile failure was observed; at potentials of -0.25, -0.2, -0.1 and 0 $V_H$ mainly IGSCC was observed. At 0 $V_H$ broad and shallow pits were observed on the side surface. These fractographs for B-16 stainless steel are shown in Figure 94.
Figure 91  SEM fractographs for A-20 stainless steel
  a Ductile failure at \(-0.2\) \(V_H\).
  b IGSCC at \(-0.1\) \(V_H\).
  c IGSCC at \(-0.06\) \(V_H\).
  d Secondary cracks at \(-0.06\) \(V_H\).
  e IGSCC plus TGSCC at \(0.1\) \(V_H\).
  f Pitting at \(0.1\) \(V_H\).
Figure 91
Figure 92  SEM fractographs for B-3 stainless steel
a Ductile failure at $-0.4\ V_H$.
b IGSCC at $-0.3\ V_H$.
c IGSCC at $-0.2\ V_H$.
d IGSCC at $-0.1\ V_H$.
e Secondary cracks at $-0.1\ V_H$.
f IGSCC at $0.1\ V_H$. 
Figure 93 SEM fractographs for B-8 stainless steel
a Ductile failure at \(-0.4 \, V_H\).
b IGSCC at \(-0.3 \, V_H\).
c IGSCC at \(-0.2 \, V_H\).
d IGSCC at \(-0.1 \, V_H\).
e IGSCC at \(0 \, V_H\).
f Pitting at \(0 \, V_H\).
Figure 94 SEM fractographs for B-16 stainless steel
a Ductile failure at -0.3 \( V_H \).
b IGSCC at -0.25 \( V_H \).
c IGSCC at -0.2 \( V_H \).
d IGSCC at -0.1 \( V_H \).
e IGSCC at 0 \( V_H \).
f Pitting at 0 \( V_H \).
Figure 94
For B-24 stainless steel at $-0.4 \ V_H$, which is below $E_{SCC}$, ductile failure was observed; and at potentials of $-0.3$, $-0.2$ and $0 \ V_H$ mainly IGSCC was observed. At $0 \ V_H$ broad and shallow pits were observed on the side surface. These fractographs for B-24 stainless steel are shown in Figure 95.

For C-4 stainless steel at $-0.4 \ V_H$, which is below $E_{SCC}$, ductile failure was observed; at potentials of $-0.1$ and $-0.05 \ V_H$ mainly IGSCC and small areas of ductile dimples were observed on the fracture surface. The ratio of IGSCC area to ductile area increased with increasing potential from $-0.1$ to $-0.05 \ V_H$. At both these potentials $-0.1$ and $-0.05 \ V_H$ secondary intergranular cracks were observed on the side surface. At $0 \ V_H$ the fracture mode was mainly TGSCC; also broad and shallow pits were observed on the side surface. These fractographs for C-4 stainless steel are shown in Figure 96.

For C-20 stainless steel at open circuit and $-0.4 \ V_H$, which are below $E_{SCC}$, ductile failure was observed; at potentials of $-0.3$, $-0.2$ and $-0.1 \ V_H$ mainly IGSCC and small areas of ductile dimples were observed on the fracture surface. The ratio of IGSCC area to ductile area increased with increasing potential. At $-0.1 \ V_H$ secondary intergranular cracks were observed on the side surface. At $0.1 \ V_H$ the fracture mode was partly TGSCC which initiated and grew independently; also broad and shallow pits were observed on the side surface. These fractographs for C-20 stainless steel are shown in Figure 97.

From the detailed presentation of the fractography, it is seen that in general at potentials below $E_{SCC}$ ductile failure was observed. At potentials above $E_{SCC}$, mainly IGSCC and small areas of ductile dimples
Figure 95  SEM fractographs for B-24 stainless steel
a Ductile failure at $-0.4 \ V_H$.
b IGSCC at $-0.3 \ V_H$.
c IGSCC at $-0.2 \ V_H$.
d IGSCC at 0 $V_H$.
e Pitting at $0^\prime \ V_H$. 
Figure 96  SEM fractographs for C-4 stainless steel
a Ductile failure at $-0.4 \ V_H$.
b IGSCC at $-0.1 \ V_H$.
c Secondary cracks at $-0.1 \ V_H$.
d IGSCC at $-0.05 \ V_H$.
e Secondary cracks at $-0.05 \ V_H$.
f TGSCC at $0 \ V_H$.
g Pitting at $0 \ V_H$. 

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Figure 96
Figure 97 SEM fractographs for C-20 stainless steel
a Ductile failure at open circuit.
b Ductile failure at \(-0.4\ V_H\).
c IGSCC at \(-0.3\ V_H\).
d IGSCC at \(-0.2\ V_H\).
e IGSCC at \(-0.1\ V_H\).
f Secondary cracks at \(-0.1\ V_H\).
g IGSCC plus TGSCC at \(0.1\ V_H\).
h Pitting at \(0.1\ V_H\).
Figure 97
were observed, with the ratio of IGSCC areas to ductile area increasing with increasing potential; secondary intergranular cracks being observed on the side surface occasionally. However, at high potentials the fracture mode was partly IGSCC and partly TGSCC, which initiated and grew independently, and broad and shallow pits were observed on the side surfaces, due to the breakdown of passivity at these high potentials.

5.2.2.4 Effect of Strain Rate on SCC Susceptibility

Figure 98 shows the effect of strain rate on SCC of A-20 stainless steel in 0.01M NaCl at 250°C, at an applied potential of 0 mV SHE, in which the elongation to fracture and area fraction of ductile failure in the fracture surface are plotted as a function of strain rate. It is seen that there is minimum in the curve, which is at a strain rate of 2x10⁻⁶ per second, which was the strain rate employed in all the SSRTs of this investigation to study the effect of nitrogen, carbon, potential, and environment, on the susceptibility to SCC of AISI 304 SS. The shape of this curve has an important significance in explaining the mechanism of SCC, which will be discussed in the next Chapter.

5.2.2.5 Effect of Strain Rate on Fracture Morphology

Figure 99 shows that at a low strain rate of 5x10⁻⁷ per second the crack has been arrested, but at an intermediate strain rate of 2x10⁻⁶ per second SCC has occurred, while at high strain rates of 10⁻⁵ and 10⁻⁴ per second ductile failure has occurred. This observation is consistent with the results shown in Figure 98. The significance of these observations in explaining the mechanism of SCC will be discussed later.
Figure 98  Elongation to failure and area fraction in fractured surface vs strain rate for A-20 steel.
Figure 99 Effect of on fracture morphology
a Crack is arrested at a low \(= 5 \times 10^{-7} /s\).
b SCC has occurred at an intermediate \(= 2 \times 10^{-6} /s\).
c Ductile failure has occurred at a high \(= 10^{-5} /s\).
d Ductile failure has occurred at a higher \(= 10^{-4} /s\).
Chapter VI

DISCUSSION

In this chapter the emphasis will be on correlating the various sensitization studies with each other, explaining the mechanisms involved for the effects of nitrogen and carbon on sensitization, correlating the various SCC studies with each other, comparing the SCC behavior in sulphate and chloride solutions, explaining the SCC mechanisms involved, and finally correlating the sensitization and SCC results.

6.1 Correlation Between Various Sensitization Studies

6.1.1 Correlation Between the EPR Tests and the Thermodynamic Model

The EPR tests showed that nitrogen up to 0.16 wt.% retards sensitization while nitrogen of 0.25 wt.% does not. This correlates well with the results of the thermodynamic model which shows that nitrogen additions up to 0.16 wt.% shift the TTS diagrams to larger times. The model is valid only for lattice diffusion controlled growth of Cr$_{23}C_6$, and is not valid at 0.25 wt.% nitrogen because of discontinuous precipitation of Cr$_{23}C_6$ (246) and the possibility of precipitation of Cr$_2N$ (9). Both the EPR tests and the thermodynamic model show that carbon is detrimental and promotes sensitization.

Even though the results of the EPR tests and the thermodynamic
model agree qualitatively they do not agree quantitatively. The reason for this is that the results of the EPR test are for a DOS of 5%, which is compared with the results of the thermodynamic model for a chromium depletion zone of less than 13 wt.% chromium of width 200 Å. This comparison has some justification because the stainless steel is said to be sensitized only when there is a chromium depleted zone of less than 13 wt.% chromium of a width larger than about 200 Å (46). In the EPR test a DOS of 5% seems to indicate the onset of sensitization, since Majidi and Streicher (141) observed a minimum DOS of about 7% for obtaining a ditch structure in the oxalic acid etch test for AISI 304 SS. The quantitative discrepancy between the EPR tests and the thermodynamic model is also due to the various reasonable assumptions made in the development of the model, which lead to certain limitations; the model is applicable only for lattice diffusional controlled growth of Cr$_{23}$C$_6$ and not for discontinuous precipitation of Cr$_{23}$C$_6$ or for precipitation of Cr$_2$N. Moreover the effect of the various alloying elements other than nitrogen, carbon, chromium and nickel in the stainless steel are not considered in calculating the activity coefficients of carbon and chromium, due to lack of data in some cases and also to keep the model simple. This assumption is reasonable because most of the other alloying elements are present in small quantities and, more importantly, their level is almost the same in all the steels. Their effect, if any, would be the same on all the steels, which would not lead to any wrong conclusions while comparing the various steels to determine the effect of nitrogen or carbon on sensitization. The validity of this assumption is shown in Table 6 in which the time for
sensitization at 650°C is calculated using the thermodynamic model.

Table 6
Time (minutes) for sensitization at 650°C calculated using the thermodynamic model for various compositions of the B series steels.

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Cu</th>
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<td>0.410</td>
<td>8.490</td>
<td>19.27</td>
<td>0.360</td>
<td>0.160</td>
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<tr>
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<td>0.008</td>
<td>0.410</td>
<td>8.490</td>
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<td>0.360</td>
<td>0.160</td>
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Effect of minor variations in carbon

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<tr>
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<td>1.770</td>
<td>0.034</td>
<td>0.007</td>
<td>0.460</td>
<td>8.590</td>
<td>18.87</td>
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<td>0.160</td>
<td>0.040</td>
<td>72</td>
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<td>0.028</td>
<td>0.008</td>
<td>0.410</td>
<td>8.630</td>
<td>18.80</td>
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<td>0.160</td>
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<tr>
<td>0.046</td>
<td>1.370</td>
<td>0.030</td>
<td>0.008</td>
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<td>18.90</td>
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Effect of minor variations of all elements

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<td>18.90</td>
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Effect of nitrogen

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<td>0.380</td>
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</tr>
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</table>

From Table 6 it is seen that minor variations in carbon (from 0.043 to 0.053 wt.% which is the most detrimental element, do not change the time for sensitization at 650°C by more than 9 minutes; compared to nitrogen additions of 0.04 to 0.16 wt.%, which delay the time for
sensitization at 650°C by about 30 minutes. It is also seen that minor variations of all the elements in the steel do not affect the time for sensitization at 650°C by more than 2 minutes, while the nitrogen additions up to 0.16 wt.% delay the time for sensitization at 650°C by about 30 minutes.

6.1.2 Correlation Between the Thermodynamic Model and the AEM Investigation

The thermodynamic model showed that nitrogen increases \( X_{Cr}^i \) and carbon decreases \( X_{Cr}^i \). This correlates well with the results of the AEM investigation, which show that nitrogen increases the grain boundary chromium concentration, while carbon decreases it. The grain boundary chromium concentration is equal to \( X_{Cr}^i \) because AEM results show no measurable chromium gradient in the grain boundary (88, 246), due to the high grain boundary diffusivity of chromium. However, the AEM values for \( X_{Cr}^i \) are consistently higher than the thermodynamically calculated values, due to the effect of electron beam broadening in the AEM samples. When this effect is considered the agreement between the values of \( X_{Cr}^i \) obtained using the two techniques is improved. However what is important is the qualitative agreement between the two techniques in showing that nitrogen increases \( X_{Cr}^i \) and carbon decreases \( X_{Cr}^i \). The AEM investigation also showed that at 0.25 wt.% nitrogen \( \text{Cr}_2\text{N} \) precipitates discontinuously (246) and therefore the thermodynamic model is not valid for this nitrogen level. Precipitation of \( \text{Cr}_2\text{N} \) was not observed in this investigation (246), though it has been observed by other investigators (9) in austenitic stainless steels containing nitrogen.
6.1.3 Correlation Between the Kinetic Model and Other Sensitization Studies

The kinetic model showed that nitrogen additions decreased the width of the chromium concentration profiles across the grain boundary, thus decreasing the width of the chromium depleted zone; and that carbon increased the width of the chromium depleted zone. The kinetic model is valid only for lattice diffusion limited growth of \( \text{Cr}_2\text{C}_6 \). This correlates well with the results of the EPR tests which show that nitrogen additions up to 0.16 wt.% retard sensitization, and carbon is detrimental and promotes sensitization. The EPR test is sensitive to both the width of the chromium depleted zone and the amount of chromium depletion, i.e. the depth of the chromium concentration profile across the grain boundary. Since nitrogen additions decrease the width of the depleted zone (as shown by the kinetic model) and increase \( X^i_{\text{Cr}} \) (as shown by the thermodynamic model and the AEM investigation), the EPR test is expected to show retardation of sensitization with nitrogen additions up to 0.16 wt.% for which these theoretical models are valid; this is indeed observed. Similarly, since carbon additions increase the width of the depleted zone (as shown by the kinetic model) and decrease \( X^i_{\text{Cr}} \) (as shown by the thermodynamic model and the AEM investigation), the EPR test is expected to show promotion of sensitization with carbon additions, which is indeed observed.

It is seen that when the chromium concentration profiles calculated using the kinetic model are compared with the profiles obtained using the AEM, the latter show a higher chromium concentration both at the
boundary and into the lattice. The reason for this discrepancy is the broadening of the electron beam in the AEM sample giving rise to higher X-ray counts. The value of the grain boundary chromium concentration is especially sensitive to the beam broadening effect. So when the grain boundary chromium concentration obtained by the kinetic model and the AEM investigation was matched the two chromium concentration profiles showed a better agreement. This agreement was further improved by considering the effect of the electron beam broadening by using the mathematical model.

6.2 Effect of Nitrogen on Sensitization

From the results presented it is seen that:

1) nitrogen additions up to 0.16 wt.% shift the TTS diagrams to longer times and hence retard sensitization, while nitrogen of 0.25 wt.% does not retard sensitization,

2) nitrogen additions up to 0.16 wt.% increase $X_{Cr}^*$,

3) nitrogen additions up to 0.16 wt.% decrease the width of the chromium depleted zone, and

4) nitrogen of 0.25 wt.% causes a very wide chromium depleted zone because of the discontinuous precipitation of Cr$_{23}$C$_6$, resulting in grain boundary migration leaving very wide chromium depleted regions behind them (246).

These results were obtained using a wide variety of techniques: electrochemical, theoretical and electron-optical; all of which yielded qualitatively similar results which correlated well with each other. The retardation effect of nitrogen on sensitization agrees with findings of
other investigators, who used techniques other than the ones used in the present investigation:

1) Eckenrod and Kovach (7) used metallographic techniques to show that nitrogen additions up to 0.16 wt.% retards sensitization,
2) Briant et al. (8) used the modified Strauss test to show that nitrogen additions (the maximum nitrogen level in their study was 0.12 wt.%) to high purity AISI 304 SS delays sensitization,
3) Mulford et al. (9) used the modified Strauss test to show that nitrogen additions (the maximum nitrogen level in their study was 0.13 wt.%) to commercial purity AISI 304 stainless steel delays sensitization.

Briant et al. (8) and Mulford et al. (9) suggested that the observed improvements could occur by a number of mechanisms:

1) Retardation of the nucleation and/or growth of the carbides,
2) Changes in the activities of chromium and carbon in equilibrium with the carbide,
3) Changes in the ease of passivation of the alloy so that more chromium depletion is required to cause sensitization, and
4) Prevention of martensite formation upon quenching.

The last two mechanisms were discounted by them (8,9) since there is lack of evidence for these. They (8,9) did not consider the changes in the activities of chromium and carbon. They (8,9) showed evidence that nitrogen segregates to the grain boundaries and hence retarded the nucleation and/or growth of the carbides. While nitrogen segregation to the grain boundaries was not studied in the present investigation, the effect of nitrogen on the activities of chromium and carbon in
equilibrium with the carbides was studied, using the thermodynamic model presented in Chapter 3. The thermodynamic model showed that nitrogen additions increase $X_{Cr}^i$. An increase in $X_{Cr}^i$ would decrease the chromium concentration gradient between the austenite matrix and the carbides at the grain boundaries, and hence retard the growth of the carbides. An increase in $X_{Cr}^i$ would also mean an increase in the effective chromium content and hence it would retard sensitization. There is no direct evidence that suggests that nitrogen changes the growth kinetics from diffusion control to interface control or mixed control. But this mechanism is a possibility because 1) in general interface or mixed control growth rates are less than diffusion control growth rates, and 2) for interface or mixed control the chromium concentration at the carbide/austenite would be higher than the equilibrium value (this was observed in this investigation but the discrepancy in the two values was partly accounted for by the effect of the electron beam broadening in the AEM samples). This mechanism would certainly operate if the nitrogen which segregates to the grain boundaries at which carbides are precipitated forms a shell around the carbides, which would act as a barrier for the transport of chromium from the austenite matrix into the carbide across the austenite-carbide interface. It can be inferred from the results of this investigation that nitrogen additions increase $X_{Cr}^i$ and decrease the width of the chromium depleted zone, thereby retarding sensitization because sensitization is due to chromium depletion (amount and width) at and adjacent to the grain boundaries.

An interesting observation of the sensitization studies, is the very wide chromium depletion for the steel containing 0.25 wt.%
nitrogen, which is due to discontinuous precipitation of the carbides resulting in grain boundary migration. The reason for this observation may be due to segregation of nitrogen to the grain boundaries and its subsequent precipitation, and the resultant migration/bowing of the grain boundaries to regions of high nitrogen levels, which would lead to overall energy reduction. Moreover the role of interfacial energy according to the Tu-Turnbull model and the chemical free energy according to the Fournelle-Clark model cannot be discounted.

6.3 **Effect of Carbon on Sensitization**

From the results presented it is seen that:

1) Carbon additions shift the TTS diagrams to shorter times and hence promotes sensitization,

2) Carbon additions decrease $X_{Cr}^i$, and

3) Carbon additions increase the width of the chromium depleted zone.

These results were obtained using a wide variety of techniques: electrochemical, theoretical and electron-optical; all of which yielded qualitatively similar results which correlated well with each other. The detrimental effect of carbon on sensitization agrees with findings of various other investigators, who used other techniques than employed in the present study, for example:

1) Cihal (116) used the acid copper sulphate test to show that carbon additions shift the TTS diagrams to shorter times, and hence promotes sensitization.

2) Weiss and Stickler (251) used electron microscopy to show that
carbon additions shift the carbide precipitation curves to shorter times, and hence promotes sensitization.

The detrimental effect of carbon is obvious because sensitization is due to precipitation of $\text{Cr}_2\text{C}_6$ and the associated chromium depletion; and increasing carbon would lead to greater amounts of $\text{Cr}_2\text{C}_6$ precipitation. Based on the theoretical models it was shown that carbon decreases $X_{\text{Cr}}^i$ and increases the width of the chromium depleted zone, both of which would lead to greater amounts of sensitization.

6.4 Correlation Between Various SCC Studies

6.4.1 High Temperature Sulphate Solutions

Anodic polarization tests showed that it was not possible to observe any influence of nitrogen on the anodic polarization behavior, and no effects were seen which would explain or predict the observed SCC performance. However, the sensitized stainless steels had higher passive current densities compared to the solution annealed steels; and in the SSRTs it was the sensitized steels which underwent SCC, not the solution annealed steels. The applied potential of 0 V$_H$ in the SSRTs, corresponds to a potential in the passive range of the stainless steels, so the SSRT specimens were covered by an oxide film during the test.

The SSRTs showed that nitrogen up to 0.16 wt.% increases the normalized elongation to fracture, which is the parameter used to define the SCC resistance, but at 0.25 wt.% the normalized elongation to fracture decreases. This result correlates well with the SEM observations of decreasing IGSCC areas in the fracture surface up to 0.16 wt.% nitrogen, and the occurrence of TGSCC at 0.25 wt.% nitrogen.
The occurrence of TGSCC at 0.25 wt.% nitrogen, also correlates with the TEM studies, which showed that the dislocation structure changes from a cellular to a planar array of mobile dislocations with increasing nitrogen additions, making the steel with 0.25 wt.% nitrogen prone to TGSCC. The correlation between the occurrence of TGSCC and the presence of a planar array of mobile dislocation structure has been observed by various investigators (15, 17, 195). The reason for nitrogen promoting a planar array of mobile dislocation structure is the decrease in stacking fault energy with nitrogen additions (15, 195-197), which restricts cross slip and, therefore, promotes planar dislocation glide rather than cellular dislocation tangles (17).

6.4.2 **High Temperature Chloride Solutions**

Anodic polarization tests showed that at high potentials the breakdown of passivity occurs. This result correlates with the occurrence of TGSCC in the fracture surface and pitting on the side surfaces of the SSRT specimens at high applied potentials, observed using the SEM. The anodic polarization tests also showed that nitrogen up to 0.16 wt.% decreases the passive current density, while nitrogen of 0.24 wt.% does not. This result is consistent with that of Eckenrod and Kovach (7), who observed lower corrosion rates up to 0.16 wt.% nitrogen, but not at 0.25 wt.% nitrogen, in the Huey tests. These results correlate well with SSRTs, which show that at an applied potential of -0.3 $V_H$ which is in the passive range, the SCC resistance increases up to 0.16 wt.% nitrogen, while at 0.24 wt.% nitrogen SCC resistance starts to decrease.
There is also a good correlation between the SSRTs and the SEM observations; as the normalized elongation to failure decreased in the SSRTs, the amount of IGSCC area in the fracture surface observed using the SEM increased. When the normalized elongation to failure increased at high potentials in the SSRTs, TGSCC was observed in the fracture surface using the SEM.

6.5 Comparison Between SCC Behavior in Sulphate and Chloride Solutions

While the anodic polarization curves in sulphate solutions exhibit a transpassive peak, in chloride solutions a breakdown of passivity is observed at high potentials. This is due to the occurrence of pitting in chloride solutions. In both sulphate and chloride solutions the sensitized stainless steels show higher current densities compared to the solution annealed stainless steels. This result is consistent with the results of Indig and Vermilyea (236) and Kushiya (237).

In the SSRTs at an applied potential of $0 \text{ V}_{\text{NHE}}$, the normalized elongation to failure is higher in sulphate solutions compared to chloride solutions. In sulphate solutions it is between about 0.2 - 0.7, while in chloride solutions it is about 0.1 - 0.5. This shows that the chloride solution is much more aggressive than the sulphate solution. Cragnolino et al. (23) observed similar results. They (23) observed that the normalized elongation to failure of AISI 304 SS, at an applied potential of $0 \text{ V}_{\text{NHE}}$, was about 0.4 in sulphate solutions, while it was about 0.1 in chloride solutions. They (23) obtained the same $E_{\text{SCC}}$ in both sulphate and chloride solutions, but the normalized elongation to
failure at potentials above $E_{SCC}$ was higher in sulphate compared to chloride solutions. In the present investigation $E_{SCC}$ was not determined in sulphate solutions. Poznansky and Duquette (30) also obtained similar results; even though they obtained the same $E_{SCC}$ in both sulphate and chloride solutions, they obtained high crack propagation rates at potentials above $E_{SCC}$ in chloride solutions. They (30) suggest that the chlorides contribute to the process of crack propagation by participating in anodic reactions at the grain boundaries.

IGSCC occurs in the passive range in both the sulphate and chloride solutions, but in the latter a breakdown potential of about $0 \, V_H$ is observed. Under potentiostatic conditions a significant increase in current density is detected above the breakdown potential, indicating the occurrence of pitting. The pitting was broad and shallow, unlike the typical pitting that would be obtained at lower temperatures in chloride solutions. IGSCC also occurs at potentials above the breakdown potential but it is accompanied with TGSCC. No increase in current density is observed during the crack propagation at potentials between $-0.3$ to $0 \, V_H$, where in general only IGSCC occurred. The same result was observed in sulphate solution in which the SSRTs were carried out at only $0 \, V_H$. These results indicate that the current response of the strained specimen is basically that of the repassivated surface, under these very slow straining conditions employed. All these above results are consistent with those obtained by Cragnolino et al. (23). Even though TGSCC was observed in the high nitrogen (0.25 wt.%) stainless steel in sulphate solution, it is different from the TGSCC that was observed at potentials above the breakdown potential in chloride solution. This
aspect is discussed in more detail in the next section on SCC mechanisms.

The occurrence of IGSCC in both sulphate and chloride solutions in the passive range is explained in terms of the poor properties of the oxide film at high temperatures. Vermilyea (252) showed that thick and less protective films are formed on the chromium depleted area along grain boundaries, so IGSCC occurs easily. The thick and less protective film also facilitates the broad and shallow pitting that was observed at potentials above the breakdown potential in chloride solutions. The same results were obtained by Cragnolino et. al. (23) and Lin et. al. (24).

6.6 SCC Mechanisms

From the SCC studies it is seen that sensitized AISI 304 SS containing nitrogen is susceptible to IGSCC in dilute aqueous sulfate and chloride solutions over a broad range of potentials. A critical potential for IGSCC \( E_{\text{IGSCC}} \) exists which is dependent on the DOS. These results are consistent with those of Cragnolino et. al. (23), Lin et. al. (24), Cragnolino and Macdonald (213), Poznansky and Duquette (30,31); all of them observed that \( E_{\text{IGSCC}} \) is dependent on DOS in AISI 304 SS. These investigators (24,30,213) have used film rupture, followed by anodic dissolution of the chromium depleted regions, as the SCC mechanism to explain their results. The results of the present investigation are also consistent with the film rupture/anodic dissolution mechanism. According to the classification in Table 1, this mechanism falls under the category of strain-assisted active path mechanism. The above investigators (24,30,213) have discounted the
pre-existing active path mechanisms, because straining is required to produce mechanical rupture of the passive film before SCC can occur, since no IGC was detected on unstressed samples (24,213), and the breakdown of the passive film on the unstressed metal occurs only in the presence of aggressive ions like chlorides at potentials higher than the breakdown potential (24,30,213). The hydrogen adsorption related mechanisms are discounted based on the effect of strain rate on SCC shown in Figures 98 and 99. If this mechanism was to operate then Figure 98 would be 'S' shaped, with low elongation to failure and high area of SCC in the fracture obtained at very low strain rates. The reason for this is that hydrogen adsorption related mechanisms do not require a film rupture event, but occur due to occluded hydrogen in the steel; as the testing period is increased by reducing the strain rate, the specimen becomes more susceptible to hydrogen cracking (253). Moreover the hydrogen adsorption related mechanisms apply in general to cracking at cathodic potentials, and not at the anodic applied potentials used in this investigation.

According to the film rupture/anodic dissolution model (24,30,213) the passive film is continuously being ruptured in the SSRT. After film rupture, the film on the grain matrix is easily repaired due to a faster repassivation rate, but at the grain boundaries which are depleted of chromium, the higher dissolution rate coupled with a lower repassivation rate confines the attack to these areas. Lin et. al. (24), Cragnolino and Macdonald (213) have shown that the establishment of appropriate electrochemical conditions at the crack tip in terms of potential will determine whether or not a crack will be arrested or propagated. They
(24,213) showed that the crack can be arrested by switching the potential to below $E_{\text{IGSCC}}$ and the crack can be propagated by switching the potential back to above $E_{\text{IGSCC}}$. They (24,213) also showed that a propagating crack can be arrested, by decreasing the corrosion potential of the specimen to a value lower than $E_{\text{IGSCC}}$, as a result of injecting a mixture of hydrogen and nitrogen gas into the system. Only above $E_{\text{IGSCC}}$ do the suitable conditions for crack initiation and propagation exist.

If the potential is below $E_{\text{IGSCC}}$, the environment at the crack tip is not aggressive, so the cracks remain inactive due to formation of a passive film, and the specimen fails in a ductile mode. If the potential is higher than $E_{\text{IGSCC}}$, the rate of metal dissolution ($M = M^{+n} + ne^-$) is enhanced. Due to hydrolysis of the metal cations, hydrogen ions will be produced and an oxide will be deposited on the walls of the crack ($2\text{Cr}^{+3} + 3\text{H}_2\text{O} = \text{Cr}_2\text{O}_3 + 6\text{H}^+$). Most of the oxide is $\text{Cr}_2\text{O}_3$ because the solubility limit of $\text{Cr}^{+3}$ is much smaller than the solubility limits for both $\text{Ni}^{+2}$ and $\text{Fe}^{+2}$. The high aspect ratio of the crack is also maintained by the faster repassivation of the crack walls which are composed mainly of the of the non-depleted alloy. The acidification at the crack tip will lead to further dissolution and cause crack propagation, because in the presence of such an aggressive local environment a passive film cannot form at the crack tip. The electroneutrality of the solution is maintained by the migration of $\text{Cl}^-$, $\text{SO}_4^{2-}$ and $\text{OH}^-$ into the crack, while $\text{Fe}^{+2}$, $\text{Cr}^{+3}$ and $\text{H}^+$ leave the crack. With increasing applied potential the rate of metal dissolution at the crack tip increases, by withdrawing electrons at a faster rate from the dissolving crack tip area, which is further assisted by the continuous straining of the metal. At the
counter electrode the cathodic reaction takes place in which hydrogen is evolved \((2\text{H}_2\text{O} + 2e^- = 2\text{OH}^- + \text{H}_2)\). When the electrode potential of the metal inside the crack is lower than the hydrogen equilibrium potential, a cathodic reaction of hydrogen evolution occurs inside the crack \((2\text{H}^+ + 2e^- = \text{H}_2)\). This reaction limits the drop of pH inside the crack. All these processes are illustrated schematically in Figure 100.

Based on the activation energy determined by plotting the average intergranular crack propagation rate as a function of reciprocal temperature, Lin et al. (24), Cragnolino and Macdonald (213) suggested that the dissolution at the crack tip is limited by the rate of diffusion of anions into the crack, and cations and other corrosion products out of the crack. Poznansky and Duquette (30), and Ford (155) have also suggested the same.

In summary, according to the film rupture/anodic dissolution model (24, 30, 213) after the passive film is ruptured, it is repaired on the matrix, but not at the grain boundary where the cracks initiate. At potentials below \(E_{\text{IGSCC}}\) the environment at the crack tip is not aggressive and the cracks remain inactive. At potentials above \(E_{\text{IGSCC}}\) electrons are withdrawn at a fast rate from the dissolving crack tip, the solution inside the crack becomes acidic due to hydrolysis, \(\text{Cl}^-\) and \(\text{SO}_4^{2-}\) migrate towards the crack tip to maintain electroneutrality, as a result the solution in the crack becomes concentrated. The dissolution at the crack tip becomes limited by the rate of diffusion of reactants and/or products into and out of the crack.

Although the film rupture/anodic dissolution mechanism is valid for IGSCC in both sulphate and chloride solutions, TGSCC in both these
Figure 100 Schematic diagram illustrating the mechanism of IGSCC of AISI 304 SS in high temperature aqueous solutions (30)
solutions are different. It was shown that in sulphate solutions TGSCC was observed at 0.25 wt.% nitrogen; SEM examination showed that the cracks initiated and propagated intergranularly to some depth and then grew transgranularly. But in chloride solutions TGSCC was generally observed for most compositions at high applied potentials; SEM examination showed that intergranular and transgranular cracks initiated simultaneously at different places on the surface and grew independently. So the mechanism for TGSCC in sulphate and chloride solutions are different.

The reason for TGSCC at 0.25 wt.% nitrogen in sulphate solutions is due to planar array of mobile dislocations along parallel slip planes observed in this steel. In contrast at a low nitrogen level of 0.04 wt.% the dislocations form a cellular structure. The decrease in stacking fault energy with nitrogen additions (15,196,197) promotes a planar array of dislocation structure. Therefore cross slip becomes difficult, dislocations are confined to their slip planes and increase the height of slip steps, and TGSCC occurs easily (195). A coarse slip step forms on the grain surface at the IGSCC tip, if a slip plane with a high density dislocation pile-up intersects the grain surface. This newly developed slip step is attacked, since the solution in the crack is concentrated and prevents passivation of the slip step. The TGSCC thus initiated on the grain surface can propagate because coarse slip steps are continuously formed, due to the high stress concentration at the crack tip and the concentrated solution at the crack tip. As the crack reaches the next grain boundary it reverts to intergranular in character because the grain boundary offers a more active passage as a result of
chromium depletion. A schematic diagram illustrating this mechanism is shown in Figure 101. This explains why TGSCC areas are found to be dispersed in IGSCC regions in the fracture surfaces of the high nitrogen steels.

In chloride solutions most of the steels undergo both TGSCC and IGSCC at high applied potentials, both of which initiated simultaneously at different places and grew independently. At high applied potentials a competition between crack initiation at the grain matrix and at the grain boundary occurs. Due to pitting that occurs at these high potentials, which is above the breakdown potential, cracks initiate from the bottom of the pits in the grain matrix. Cracks also initiate at the grain boundaries. For this reason both TGSCC and IGSCC were observed at high applied potentials in chloride solutions. Unlike in sulphate solutions, TGSCC was not observed in chloride solutions, at applied potentials in the passive range, in the 0.25 wt.% nitrogen steel. The reason for this observation is that chlorides contribute to the process of intergranular crack propagation by participating in anodic reactions at the grain boundaries. As suggested by Poznansky and Duquette (30) this reason also explains why the normalized elongation to failure is always lower in chloride solutions compared to sulphate solutions.

6.7 Correlation Between SCC and Sensitization Studies

6.7.1 High Temperature Sulphate Solutions

The SCC studies showed that nitrogen up to 0.16 wt.% decreases susceptibility to IGSCC; in the SSRTs the normalized elongation to failure increased, and SEM examination showed that the IGSCC area
Figure 101  Schematic diagram illustrating the mechanism of TGSCC of 0.25 wt.% nitrogen steel in sulphate solutions.
decreased with nitrogen additions up to 0.16 wt.%. This tendency is similar to the effect of nitrogen on sensitization. The results of the sensitization studies carried out during this investigation show that nitrogen additions retard sensitization. Therefore it is seen that a good correlation exists between the susceptibility to IGSCC and the DOS. This result is consistent with the results of other investigators (22,25,32,153), who showed that susceptibility to IGSCC increases in high temperature water with increasing DOS. The same result was obtained by other investigators (23,30,31), in high temperature aqueous sulphate and chloride solutions.

It was observed that the solution annealed steels had a high resistance to SCC irrespective of their nitrogen content. This observation again indicates that sensitization is responsible for IGSCC in high temperature sulphate solutions. Therefore decreasing DOS should decrease susceptibility to IGSCC, which was indeed observed.

6.7.2 High Temperature Chloride Solutions

The anodic polarization tests showed that nitrogen additions up to 0.16 wt.% decreased the passive current density. This correlates well with the sensitization studies, which show that nitrogen additions up to 0.16 wt.% retard sensitization. This good correlation between the passive current density and DOS is consistent with the results of Poznansky and Duquette (31), who showed that the passive current density decreased, and the passivity breakdown potential increased, with decreasing DOS in the system AISI 304 SS/deareated 1N NaCl aqueous solution adjusted to pH 4 with HCl at room temperature. They (31)
suggested that $x_{Cr}^{i}$ is the major factor which determines both the passivity breakdown potential and $E_{IGSCC}$. The correlation between DOS and $E_{IGSCC}$ is examined next.

The SSRTs showed that nitrogen additions up to 0.16 wt.% increase $E_{IGSCC}$, while carbon additions decrease $E_{IGSCC}$. This correlates well with the sensitization studies, which showed that nitrogen additions up to 0.16 wt.% decreases the DOS, while carbon additions increases the DOS. Some authors (31,33) have suggested that $x_{Cr}^{i}$ is the major factor which determines $E_{IGSCC}$, while others (16) have suggested that the width of the chromium depleted zone is more important. This aspect could not be resolved in the present investigation, because when nitrogen increased $x_{Cr}^{i}$, it decreased the width, both of which are beneficial in decreasing the DOS; and when carbon decreased $x_{Cr}^{i}$, it increased the width, both of which are detrimental in increasing the DOS. The present investigation however shows a good correlation between $E_{IGSCC}$ and the DOS; decreasing the DOS by nitrogen additions up to 0.16 wt.% increases $E_{IGSCC}$, and increasing the DOS by carbon additions decreases $E_{IGSCC}$. This correlation is consistent with the results of Cragnolino et. al. (23), Poznansky and Duquette (31), who showed that $E_{IGSCC}$ in high temperature aqueous solutions decreased with increasing sensitizing time.

SEM examination of the fracture morphology showed that for the steel with 0.04 wt.% nitrogen, TGSCC occurred above $E_{SCC}$ for the steel with 0.04 wt.% carbon, while IGSCC occurred above $E_{SCC}$ for the steel with 0.07 wt.% carbon. Moreover $E_{SCC}$ for the steel with 0.02 wt.% carbon is higher than $E_{SCC}$ for the steel with 0.07 wt.% carbon. The reason for
these results are that the DOS of the steel with 0.02 wt.% carbon is low, while the DOS of the steel with 0.07 wt.% carbon is high. A similar correlation was observed by Poznansky and Duequette (31), who showed that as long as the DOS was low the steel was susceptible to TGSCC and once the DOS became high the steel became susceptible to IGSCC, with the shift in the fracture mode from TGSCC to IGSCC being accompanied by a decrease in $E_{SCC}$. 
Chapter VII

SUMMARY, CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

7.1 Summary and Conclusions

The present investigation can be summarized by drawing the following conclusions:

1. Thermodynamic models have been used to construct time-temperature-sensitization (TTS) diagrams for AISI 304 stainless steels with and without nitrogen additions. TTS diagrams for AISI 304 stainless steels containing nitrogen obtained using the EPR tests are also reported. AEM was used to study the microchemistry at the vicinity of grain boundaries, and its effect on sensitization of AISI 304 stainless steels containing nitrogen. The results of this investigation indicate that nitrogen additions up to 0.16 wt.% retard the sensitization kinetics by increasing the chromium concentration at the chromium carbide-austenite interface, which retards the growth of the carbides. At 0.25 wt.% nitrogen, the chromium carbides precipitate discontinuously, resulting in grain boundary migration and wider chromium depleted regions and hence sensitization is not retarded. Carbon additions promote sensitization by decreasing the chromium concentration at the chromium carbide-austenite interface, which promotes the growth of the carbides.

2. Kinetic models have been used to construct the chromium
concentration profiles across the grain boundaries of the sensitized steels and were compared with the experimental profiles obtained using the AEM. The agreement between the calculated and experimentally obtained chromium concentration profiles was improved by using the mathematical model which considers the effect of electron beam broadening. The results of the kinetic model indicate that nitrogen additions up to 0.16 wt.% decreases the DOS, by decreasing the width of the chromium concentration profiles across the grain boundaries, while carbon additions increase the DOS by increasing the width of the chromium concentration profiles across the grain boundaries.

3. SSRTs were conducted on solution annealed and sensitized AISI 304 stainless steels with varying nitrogen and carbon contents in order to study their susceptibility to SCC. The tests were conducted in deaerated 0.01M Na$_2$SO$_4$ at 250°C, at a strain rate of $2 \times 10^{-6}$ per second and an applied potential of 0 V. SEM was used to observe the fracture surfaces of the SSRT specimens. For the solution annealed stainless steel containing 0.05 wt.% carbon, the susceptibility to IGSCC remained unchanged with nitrogen additions. For the sensitized stainless steel containing 0.05 wt.% carbon, the susceptibility to IGSCC decreased with nitrogen additions up to about 0.16 wt.%; this is due to the effect of nitrogen in retarding sensitization. SEM showed that a transition from IGSCC to TGSCC occurred at higher nitrogen contents; this is due to the effect of nitrogen in promoting a planar mobile dislocation structure. Potentiodynamic polarization curves measured in the above environment were identical for both the solution annealed and sensitized conditions, but the latter showed slightly higher current densities.
Nitrogen additions had no influence on the anodic polarization characteristics. No changes were noted in the polarization curves which would explain or predict the observed SCC performance. For the sensitized stainless steels, the susceptibility to IGSCC increased with carbon additions; this is due to the effect of carbon in promoting sensitization.

4. SSRTs at various applied potentials, and potentiodynamic polarization tests, were conducted in deaerated 0.01M NaCl solution at 250°C on sensitized AISI 304 SS with varying nitrogen and carbon contents. SEM was used to observe the fracture surfaces of the SSRT specimens. SSRT results show that SCC occurs above a certain critical potential ($E_{SCC}$) which depend on the carbon and nitrogen content; $E_{SCC}$ is within -0.3 to -0 V$_H$, with nitrogen additions up to 0.16 wt.% increasing $E_{SCC}$ and carbon additions decreasing $E_{SCC}$. This indicates that the DOS is the major factor which determines $E_{SCC}$. The DOS also determines the fracture mode obtained above $E_{SCC}$; at low DOS TGSCC occurs, while at high DOS IGSCC occurs. The potential ranges at which (1) IGSCC and (2) simultaneous IGSCC, TGSCC and pitting occurred correspond to (1) the passive range and (2) potentials above the breakdown of passivity on the polarization curves. The passive current density in the polarization curves decreases with nitrogen additions up to 0.16 wt.%, this is due to the effect of nitrogen in retarding sensitization.

5. SSRTs at various strain rates were conducted in deaerated 0.01M NaCl solution at 250°C on sensitized AISI 304 SS with 0.02 wt.% carbon and 0.20 wt.% nitrogen. SEM was used to observe the fracture
morphologies of the SSRT specimens. From the shape of the elongation to failure and area fraction of SCC in the fractured surface versus strain rate curve, it is inferred that hydrogen adsorption related SCC mechanisms are not operative at the anodic potential ranges at which the SSRTs were carried out. Based on the results of this investigation, which are consistent with those of other investigators (24,30,213); the film rupture/anodic dissolution model (24,30,213) for IGSCC is the mechanism that is operative.

6. Good correlations were obtained between the various sensitization studies. The theoretical modeling, electrochemical and electron-optical studies indicate that nitrogen additions up to 0.16 wt.% are beneficial. Good correlations were also obtained between the sensitization and SCC studies; since the latter indicate that nitrogen additions up to 0.16 wt.% decrease the susceptibility to IGSCC and increase $E_{SCC}$, due to the beneficial effect of nitrogen on sensitization. So IGSCC failure of BWR piping in the future can be avoided by optimum nitrogen additions, which would control the sensitized microstructure and also maintain the corrosion potential of the stainless steel below $E_{IGSCC}$.

7.2 Suggestions for Future Work

The present investigation has clearly showed that optimum nitrogen additions mitigate the IGSCC failure of BWR piping; and has helped understand the mechanisms involved, in explaining the beneficial effect of nitrogen at optimum levels, on sensitization and IGSCC of AISI 304 SS. But there is scope for further work as listed below:
1. The thermodynamic model can be extended to incorporate the effect of all the elements in the stainless steel on sensitization. In the present investigation the stainless steel was assumed to be an Fe-Cr-Ni-C-N alloy because in the present investigation the different steels had all the other elements at a constant level, which did not affect the analysis when each steel was compared with one another.

2. In the present investigation Cr$_2$N was not observed, though other investigators (9) observed Cr$_2$N at the higher nitrogen levels. Further careful electron-optical investigations can be carried out to look for Cr$_2$N, using the carbon extraction technique. If Cr$_2$N is found to play any significant role in the higher nitrogen steels, then the thermodynamics and kinetics of Cr$_2$N precipitation can be considered in a manner similar to Cr$_{23}$C$_6$ precipitation; and its effect on sensitization can be theoretically modeled.

3. The present investigation showed that discontinuous precipitation of Cr$_{23}$C$_6$ occurs at high nitrogen levels leading to wide chromium depletion behind migrating grain boundaries. The mechanisms involved have only been postulated in the present investigation, further electron-optical investigation is necessary to determine the mechanisms involved. Auger electron spectroscopy in particular can be used to study nitrogen segregation to grain boundaries (9).

4. More information on the microchemistry, especially nitrogen and carbon concentration profiles at the vicinity of carbides at grain boundaries, is necessary to determine if nitrogen changes the Cr$_{23}$C$_6$ growth from diffusion control to interfacial or mixed control. Wave length dispersive spectroscopy can be used to investigate this aspect.
5. In the present investigation chromium concentration profiles along the grain boundaries away from an isolated carbide were neither calculated or measured. Kinetic modeling and AEM investigation of these profiles would provide further information regarding the microchemistry near the grain boundaries (49), and how it affects sensitization and SCC.

6. In the present investigation sensitization was correlated to SCC, however the microstructure (type, morphology and coherency) was not. It has been recently shown that a good correlation exists between the SCC resistance of alloy X-750 in deareated high temperature water and the type, morphology and coherency of precipitates along the grain boundaries (254).

7. TEM studies using weak beam techniques (197) are required, to find the effect of nitrogen on stacking fault energy, and correlate these to the occurrence of TGSCC.

8. The temperature dependence of the average intergranular crack propagation rate is required, to confirm that the rate limiting step during the SCC process is liquid diffusion (24). So SCC tests need to be carried out at temperatures other than 250°C used in the present investigation.

9. There are different viewpoints in literature regarding whether the applied potential (23, 24, 30, 31, 213) or the dissolved oxygen content (33, 255) is the important environmental factor in determining IGSCC resistance. Since in the present investigation SSRTs were not conducted in oxygenated environments under open circuit conditions this aspect could not be resolved. Moreover the effect of other environmental
factors like hydrogen injection into the system were not studied. Also the effect of stress factors were not studied.
APPENDICES

APPENDIX A

Program to Calculate TTS Diagrams

```plaintext
TYPE *, 'Type data Wc Wmn Wp Ws Wsi Wni Wcr Wmo Wcu Wn '
Read(5,*)Wc,Wmn,Wp,Ws,Wsi,Wni,Wcr,Wmo,Wcu,Wn
R=2.
Wf=100.-(Wc+Wmn+Wp+Ws+Wsi+Wni+Wcr+Wmo+Wcu+Wn)
D=Wc/12.+Wmn/54.94+Wp/30.97+Ws/32.06+Wsi/28.09+
1  Wni/58.71+Wcr/52.+Wmo/95.94+Wcu/63.54+Wn/14.01+
2  Wf/55.85
Xcr=(Wcr/52.)/D
Xc=(Wc/12.)/D
Xn=(Wn/14.01)/D
Xni=(Wni/58.71)/D
Xfe=(Wfe/55.85)/D
Xsi=(Wsi/28.09)/D
Xmn=(Wmn/54.94)/D
Xmo=(Wmo/95.94)/D
Xp=(Wp/30.97)/D
T=769.
DO 100 I=1,51
T=T+4.
1 gcrfe=1770.-1.5*T
gfecn=1770.-1.5*T
gcrni=-2000.+ .11202E-2*T^2-.18649E-5*T*T*T
gfecn=-6000.+ .2265E-2*T^2-.6231E-6*T*T*T
gfecn=500.-.9573B-3*T*T+.39029E-6*T*T*T
gfecn=8320.+ .58327E-2*T^2-.24859E-5*T*T*T
AT=1./(R*T))**-(Xcr*Xfe)/(Xcr+Xfe)*(Xcr*gcrfe+Xfe*gfecn)
1 Xfe*gfecn+(Xcr*Xni)/(Xcr+Xni)*(Xcr*gcrni+Xni*gnicr)
2 +(Xfe*Xni)/(Xfe+Xni)*(Xfe*gfecn+Xni*gnicr)
Ccr=(1./(R*T))**2*(2500.+ .15*T+Xfe/(Xcr+Xfe)**2)*
1 (Xcr*(Xcr+2.*Xfe)*gcrfe+Xfe*Xfe*gfecn)+
2 (Xni/(Xcr+Xni)**2)*2*(Xcr*(Xcr+2.*Xni)*gcrni+
3 Xni*Xni*gnicr))
GCXcr=AT+Ccr
Gamcr=exp(GCXcr)
IntCr=(-36736.8/T)+9.614
GCXcr=GCXcr+IntCr*Xn
GamcrN=exp(GCXcr)
Diff=.08*EXP(-29250./T)
Gfrm= -9.828E4-9.24*T
V=(-1.*Gfrm)/(R*T)
IF (V.GE.8749.8233E-2) V=8749.8233E-2
```

254
EQ = EXP(V)
ActC = EXP(ALOG(.048*Wc) + (.525 - 300./T)*Wc - 1.845 + 5100./T - (.021 - 72.4/T)*Wni + (.248 - 404./T)*Wcr - (.0102 - 9.422/T)*Wcr**2)
GamC = ActC/Xc
IntC = (1315.8/T) - .3449
GCXc = ALOG(GamC) + IntC*Xc
GamC = EXP(GCXc)
ActCN = GamC*Xc
Xcrint = ((1 - Xc - Xn)/Gamcr)*(EQ**(-.04348))*(Acte**(-.2609))
XcriN = ((1 - Xc - Xn)/GamcrN)*(EQ**(-.04348))*(ActCN**(-.2609))
Tim = 4E-12*(Xcr - Xcrint)**2/(4.*Diff*(.13 - Xcrint)**2)
TimN = 4E-12*(Xcr - XcriN)**2/(4.*Diff*(.13 - XcriN)**2)
Z = ALOG10(Tim/60.)
ZN = ALOG10(TimN/60.)
TC = T - 273.
Write(15,*)Z, TC
Write(20,*)ZN, TC
100 Continue
STOP
END
APPENDIX B

C PROGRAM TO CALCULATE Cr. CONC. PROFILE ACROSS G.B.
C
C Cm & Ci are matrix and g.b. (minimum) Cr. conc. in wt. %
C Ri=Carbide radius in cms, T=sensitization temp. (not used in this calc. since diffusion coeffient, D in cm2/sec is fed in)
C time & S are sensitization time in hrs. & sec. respectively
Type *, 'Type data Cm Ci Ri T time D'
Read (5,*) Cm,Ci,Ri,T,time,D
Write (15,22)

22 Format
(4X,'Cm',2X,'Ci',2X,'Ri',2X,'T',2X,'time',2X,'D'/)
Write (15,*) Cm,Ci,Ri,T,time,D
Write (15,21)

C R is distance from center of carbide in cms
C DIST. and X are distance from g.b. in nms and cms respectively

21 Format (4X,'DIST.',4X,'C'/)
S=time*3600.
R=Ri-10.E-7
DO 100 I=1,41
R=R+10.E-7

C U,V,W,Ui,Vi, Wi are variables used to calculate the Cr. conc., C at R from the g.b.
U=EXP(-1.*R**2/(4.*D*S))
V=R/SQRT(D*S)
W=1.-ERF(V/2.)
Ui=EXP(-1.*Ri**2/(4.*D*S))
Vi=Ri/SQRT(D*S)
Wi=1.-ERF(Vi/2.)
C=Cm+(Ci-Cm)*((U/V)-.886*W)/((Ui/Vi)-.886*Wi)
X=R-Ri
Dist=X*1.E7
Write (15,*) Dist,C

100 Continue
Stop
End
C PROGRAM TO CALCULATE Cr CONC. PROFILES CONSIDERING THE EFFECT OF BEAM BROADENING

C Cg & Cm ARE G.B. & MATRIX CONC., ALPA=HALF WIDTH OF TRUE PROFILE
C BETA=CONSTANT THAT CONSIDERS BEAM BROADENING
C BETAO=HALF WIDTH OF INCIDENT BEAM
C t=FOIL THICKNESS, N=# OF INTEGRATION STEPS
TYPE *,'TYPE DATA Cm,Cg,ALPA,BETA,BETAO,t,N'
READ (5,*) Cm,Cg,ALPA,BETA,BETAO,t,N
WRITE (15,21)
21 FORMAT (4X,'Cm',2X,'Cg',2X,'ALPA',2X,'BETA',2X,'BETAO',
2X,'t',2X,'N')
WRITE (15,*) Cm,Cg,ALPA,BETA,BETAO,t,N
C C=Cr CONC. AT DIST. X FROM G.B.
X=0.
C0=Cm-Cg
DO 100 I=1,80
C X=DIST. FROM G.B. IN NMS.
C H=WIDTH OF EACH INTEGRATION STEP
H=t/FLOAT(N)
NN=N-1
SUM=0.
DO 200 K=1,NN
C Z=DIST. ALONG THICKNESS DIRECTION OF FOIL
Z=FLOAT(K)*H
C R=ANALYTICAL EXPRESSION THAT CONSIDERS BEAM BROADENING
U=BETA*(Z**1.5)+BETAO
V=U**2+ALPA**2
W=SQRT(V)
Q=EXP(-1.*X**2/V)
R=ALPA*Q/W
SUM=SUM+R
200 CONTINUE
C Ro AND Rt ARE FIRST AND LAST TERMS OF THE SUM WHILE INTEGRATING
Uo=BETAO
Ut=BETA*(t**1.5)+BETAO
Vo=Uo**2+ALPA**2
Vt=Ut**2+ALPA**2
Wo=SQRT(Vo)
Wt=SQRT(Vt)
Qo=EXP(-1.*X**2/Vo)
Qt=EXP(-1.*X**2/Vt)
Ro=ALPA*Qo/Wo
Rt=ALPA*Qt/Wt
SUM=SUM+Ro+Rt
C AREA=AREA UNDER THE CURVE R VS Z = VALUE OF THE INTEGRATION
AREA=H*SUM/2.
\[ C_{1} = Co \times \frac{\text{AREA}}{t} \]
\[ C = C_{m} - C_{1} \]
\[ \text{Write}(15,*)X,C \]
\[ X = X + 5. \]

100 CONTINUE
STOP
END
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