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Intergranular stress corrosion cracking of nickel and iron-base alloys in high-temperature water

Shen, Yulin, Ph.D.
The Ohio State University, 1990
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INTERGRANULAR STRESS CORROSION CRACKING
OF NICKEL AND IRON BASE ALLOYS
IN HIGH TEMPERATURE WATER

DISSERTATION
Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate School of
The Ohio State University
By
Yulin Shen, B.S., M.S., M.S.

* * * * *
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To my parents, my wife, and daughter.
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INTRODUCTION

There are a number of nickel and iron based alloys used in pressurized water reactors (PWR), where the environment contains high temperature deaerated water. Many of the alloys have experienced intergranular stress corrosion cracking (IGSCC) (1-5). These alloys are used as various components in the construction of the reactor. For example, Alloy 600 is used as tubing material, X-750 as bolts, springs and guide pins, and 410 stainless steel (410SS) is used as valve stems and shafts. All of these failures occurred in highly stressed and strained regions with a cracking path predominately along grain boundaries.

For Alloys 600 and X-750, the microstructure is important to the IGSCC susceptibility in the PWR environment. A general trend exists that a susceptible heat treatment always retains more carbon in solution. However, a treatment that precipitates chromium carbides on the grain boundary retards the IGSCC. In this case the carbon activity in the matrix near the grain boundary is low. Although plenty of studies on the IGSCC of Alloy 600 have been published (2), the nature of the failure mode is still not clear.
At elevated temperatures, grain boundary cavitation is a major fracture mode of stressed metals (6). It starts from void nucleation at grain boundaries, and proceeds by void growth and linkup to the final fracture of the material. When the fracture occurs in an environment containing detrimental species such as hydrogen or oxygen, the rate of failure may be enhanced. In certain cases, the environment is aggressive enough to induce failure even without the presence of stress. Hydrogen attack (HA) in steels is a typical example, which occurs in a environment with hot high pressure hydrogen (7). Hydrogen diffuses into the metal to react with the carbon to form high pressure methane bubbles on the grain boundary. The methane bubbles grow and link up to produce fissures on the grain boundary and cause the fracture of the steels.

A comparison of the IGSCC of Alloy 600 and X-750 in the PWR and hydrogen attack in pressure vessels shows several similarities. They are:
- hydrogen present in the environment
- the IGSCC is faster in structure with more carbon in solution
- the temperature range favors the formation of methane by the reaction of hydrogen and carbon
- cracking along grain boundaries

Shewmon (8) suggested a hydrogen induced void-
linkage model for the IGSCC of Alloy 600 in a PWR environment which was later verified by Shen (9). The model proposes that the IGSCC occurs by the nucleation and growth of a fine array of grain boundary microvoids in front of an advancing crack. Nucleation of the voids is assisted by high pressure of methane, the applied stress, and the impingement of slip lines at the grain boundary. The methane gas can be formed through reaction of hydrogen generated near the crack tip and carbon supersaturated in solution as a result of heat treatment. As the voids start to grow, the high pressure methane and the applied stress drive atoms away from the void surface by boundary diffusion. The carbon in the matrix is rapidly depleted due to slow carbon diffusion, and the methane pressure rapidly drops due to the lack of carbon supply. The applied stress becomes the main driving force for the void growth. Finally the voids link up to produce the fracture.

First part of this dissertation is a continuing effort to study the hydrogen induced IGSCC of nickel based alloys in high temperature deaerated water. Four aspects of the hydrogen induced IGSCC in Alloy 600 and X-750 are studied.
1. The nucleation of grain boundary voids,
2. The effect of stress intensity on the crack growth rates of Alloy 600,
3. Verification of the void-linkage model in Alloy X-750,

On the other hand, IGSCC has been observed in the 410SS components in the PWR environment as well. The failure occurred when the material was improperly tempered with a hardness higher than $R_C \leq 26$ (5). Since the IGSCC of 410SS in high temperature water has not been studied much, the mechanism of the cracking is not clear. This alloy is used in a structure of tempered martensite. The tempering treatment softens the martensite. An improper treatment could introduce temper embrittlement of this steel at room temperature. The failures of the IGSCC in high temperature water resembles the temper embrittlement, and both type of fracture occur by a similar temper treatment. Thus, these two failures seem to be closely related. The reason for temper embrittlement of 410SS is not clear, although a number of mechanisms have been proposed. Segregation of detrimental species to the grain boundary is a prime candidate which could induce the grain boundary cracking. Hydrogen embrittlement may be another mechanism for this high strength steel.

In the second part of this dissertation, the temper embrittlement of 410SS is studied to shed some light on the mechanism of IGSCC of 410SS in a PWR environment. Two sets of experiments are conducted in this part:
1. The IGSCC tests of 410SS in high temperature deaerated water,
2. The temper embrittlement tests of 410SS at room temperature.

In Chapter I, a literature review is given for the studies on the IGSCC of Alloy 600, X-750 and 410SS in the PWR or high temperature deaerated water. Chapter II describes the experimental procedures. The results and analysis are presented in Chapter III. Chapter IV discusses the experimental results. Chapter V contains the conclusions from the present study.
CHAPTER I

LITERATURE REVIEW

This review describes the PWR environment and discusses previous observations of intergranular stress corrosion cracking of Alloy 600, and X-750 in high temperature deaerated water. Next the hydrogen induced void-linkage model for the IGSCC is discussed. Finally, a review on the IGSCC of 410SS and the temper embrittlement in martensitic steels is given.

1.1 PRESSURIZED WATER REACTOR ENVIRONMENT

PWRs contain primary and secondary side water systems (10). The primary side includes the reactor vessel, pipes connecting it to the steam generator, and the steam generator tubing. Water inside the primary system is pressurized to 15.5 MPa at a temperature up to 317°C, without boiling. In the steam generator, heat is transferred from tubes into the secondary side water where steam is generated at 288°C with a pressure of 7 MPa. The steam is then used to drive the turbine-generator.

The present study focuses on the IGSCC occurring in the primary water environment in which up to a few hundred
ppm of boric acid is added to control the reactivity changes, and lithium hydroxide is used for buffering to control the pH value (about 9 at room temperature). In the primary water, the oxygen content is below the ppb level due to overpressurized hydrogen, which is maintained to suppress radiolytic decomposition of water (11).

1.2 IGSCC IN THE PRIMARY AND DEAERATED WATER

It is well known that stress corrosion cracking occurs with a critical combination of stress, environment, and a susceptible material. IGSCC of alloys in the PWR occurs at stressed regions of various components which have been improperly heat treated. The main cracking path is along grain boundary with little or no plastic deformation. Several alloys exhibit this type of cracking, including Alloy 600, X-750, and 410SS. During the past two decades, numerous IGSCC incidents in PWR systems have been reported. For Alloy 600, the cracking occurs mostly at the U-bend tubes or the expanded tube transitions in the steam generator (1,2). For alloy X-750, cracking was observed in components such as bolts, springs, and guide pins (3,4). IGSCC was also reported at valve stems and shafts made of 410SS (12).

Of the three types of materials, the IGSCC of Alloy 600 is the most studied case due to the numerous failure incidents, while the IGSCC of 410SS has not received much attention in the PWR environment. The characteristics of
IGSCC in high temperature primary water or deaerated water/steam is summarized as follows:

a. Microstructure plays a dominant role. In both Alloy 600 and X-750, a microstructure with chromium carbides on grain boundaries is resistant to IGSCC, while a microstructure with no grain boundary chromium carbides is susceptible to IGSCC (1-3,13,14).

b. Applied or residual stresses must be present to produce cracking (2,3,9,15). Failure has not been reported to occur in a stress-free region.

c. Presence of strain or plastic deformation also aids the IGSCC of Alloy 600 (2,8,16).

d. With a small overpressure of hydrogen, the cracking is enhanced (17). That means the dissolved hydrogen may adsorb on the alloy surface and diffuse into it to assist the IGSCC. Furthermore, driving the potential to the cathodic side generates more hydrogen and enhances the IGSCC of Alloy 600 (18).

e. The cracking rate increases rapidly with temperature (2).

These characteristics indicate that hydrogen plays an important role in the IGSCC of these alloys. The following sections separately discuss factors that affect the hydrogen induced IGSCC for each alloy.
1.3 IGSCC OF ALLOY 600 IN PRIMARY AND DEAERATED WATER/STEAM

Alloy 600 is a solid solution hardened nickel based alloy which contains about 75% nickel, 15% chromium, and 9% iron. In the past, mill annealed Alloy 600 by a treatment at 900-1100°C for 30 minutes was identified as a corrosion resistant material in acidic solutions at room temperature or oxygenated water at high temperature (2). Thus mill annealed Alloy 600 was used for tubing material in PWR steam generators. Initially the performance of the material was good. However, since the first laboratory report that IGSCC was observed in the primary water or deoxygenated water (19), numerous IGSCC tube failures have occurred in PWR systems (2). IGSCC is affected by a number of factors such as microstructure, stress/strain, temperature, electrochemical potential, surface oxide, and hydrogen partial pressure in the environment. These factors are reviewed in the following paragraphs.

Annealing at low temperatures (926°C or less) produces material susceptible to IGSCC in high temperature deaerated water. Stein et al. (20) found that the microstructure contains chromium carbides inside the grains and has essentially no precipitates on the grain boundaries. On the other hand, annealing at high temperature (over 1000°C) produced more grain boundary chromium carbides and made the material more resistant to the IGSCC. The tendency that grain boundary chromium
carbides increase the IGSCC resistance of Alloy 600 was also observed by De et al. (21) and Economy et al. (17). A heat treatment near 700°C for 15 hours increased the IGSCC resistance in high temperature water environment. Examining the microstructure, they found that the chromium carbides precipitate at the grain boundary.

A treatment in the range between 600 and 750°C tends to precipitate chromium carbides on grain boundaries. Since the diffusion of chromium is slow, the region near the carbide will deplete the matrix of chromium. Thus a chromium depleted zone near the grain boundary is formed. This microstructure is conventionally called sensitized material in austenitic stainless steels and in Ni based alloys. Exposing the sensitized material to the oxygenated high temperature water will cause preferential attack of the Cr depleted zone. However, in the primary water environment, Alloy 600 with grain boundary carbides is more resistant to IGSCC than a structure without grain boundary carbides. Thus the anodic dissolution mechanism associated with the chromium depletion along the grain boundary can not explain the IGSCC in question.

In addition to microstructural factors, mechanical effects have proven to be very important. IGSCC in Alloy 600 often occurs at highly stressed or plastically deformed regions such as U-bend tubes and the expanded tube transition within the tube sheet. Laboratory reports also show that tensile stress near the yield stress is
necessary for the initiation of cracking (2). Residual stress is as effective as tensile stress in causing cracking (15). Recently, Shen (9) reported that the IGSCC cracking always occurs at the maximum biaxial tension state in reverse U-bend specimens. This is further confirmed in the slow strain rate testing in which the surface cracking is perpendicular to the loading direction. Bulischeck and van Rooyen (22) observed that cold work can reduce the initiation time and accelerate the crack growth rate. It is also reported that for cold worked materials the crack propagation rate is faster than in annealed material (2). Totsuka et al. (23) performed slow strain rate tests in simulated primary water at 350°C and reported that a cold worked hump in the sample is necessary to give IGSCC in this type of test. Shewmon (8) and Shen (9) agreed that plastic deformation plays an important role in the cracking initiation process, where slip lines impinging on the grain boundary aids the void nucleation on the grain boundary.

The IGSCC crack growth rate increases with temperature, following an Arrhenius relation. The apparent activation energy can be obtained from the slope by plotting the growth rate versus the reciprocal of temperature. A wide range of activation energies has been reported by various researchers, ranging from 74 kJ/mol (24) to 182kJ/mol (17). Using a wedge-opening loaded specimen to measure the crack growth rate, Shen (9)
obtained an activation energy at 80kJ/mol. He proposed that the activation energy could be related to the nickel grain boundary diffusion process, in which grain boundary voids grow by removing nickel atoms from void surface and depositing on the adjacent grain boundary by boundary diffusion. Graud and McIlree suggested that different activation energies may indicate that a combination of different processes contribute simultaneously to the cracking process (25).

The electrochemical potential also plays an important role as observed by Totsuka and Szklarska-Smialowska (18). They found that cathodic potentials relative to the standard electrode potential increase IGSCC in the material while anodic potentials reduces the percentage of IGSCC. This suggests that IGSCC is cathodically controlled and that hydrogen is an important factor in the cracking.

Hydrogen overpressure and oxide seemed to be important to the IGSCC, and they appeared to be closely related. Oxide is always found on the surface of the material whenever the IGSCC is observed. The composition of the oxide was identified to be mainly Cr\(_2\)O\(_3\) based (26). Although the real role of oxide is not clear, this may suggest that corrosion or oxidation is necessary for the initiation of the cracking. Moreover, in the primary water, about 0.1 MPa hydrogen overpressure is added to the water to suppress the radiolytic decomposition of water
Economy et al. (17) showed that about 11 psi of hydrogen produces the most severe cracking, while increasing the hydrogen overpressure further decreases the tendency for cracking. Shen (9) obtained similar results by changing hydrogen overpressure from 0.1, 0.5 to 0.8 MPa (STP). He confirmed that for an overpressure of hydrogen of 0.1 MPa, the cracking time was the lowest compared to the other two experiments with higher hydrogen pressure environment. In addition, he found that with an overpressure of 0.8 MPa, the oxide film on the surface is the least dark compared to the other two cases, which means the oxide is the thinnest among the three. And yet he found that the cracking time increases with the hydrogen overpressure, in which the thickness of the oxide film decreases with the hydrogen overpressure. A possible explanation for this is that higher hydrogen pressure reduces the formation of surface oxide which is the process that produces the high fugacity of hydrogen that induces IGSCC. So increasing the hydrogen overpressure decreases the supply of hydrogen and IGSCC stops.

In summary, the hydrogen induced IGSCC of Alloy 600 occurs in a structure with grain boundary chromium carbides, and the cracking is enhanced by stress, strain, hydrogen overpressure, and cathodic potential. The increases in IGSCC crack growth rate with temperature follows the Arrhenius relation.
1.4 IGSCC OF ALLOY X-750 IN PRIMARY OR DEAERATED WATER

The composition of Alloy X-750 is very similar to that of Alloy 600, except some titanium, niobium and aluminum are added to give aged hardening. Alloy X-750 has good corrosion and oxidation resistance and high creep strength up to 815°C (27). It has long been used in the aircraft engine industry for high temperature applications. The nuclear industry uses the material for bolts, springs, and guide pins in core components of PWRs. In 1970s Blanchet et al. (28) reported laboratory observation of IGSCC in X-750 in 300 and 350°C deaerated water. Later, incidents of IGSCC failures were reported in the commercial nuclear power industry (3,4).

Heat treatment and a number of other factors influence the IGSCC of Alloy X-750. For instance, stress assists the cracking, addition of alloying element and electrochemistry may have important effects, but impurity segregation and chromium depletion have little or no effect. In following sections, these factors are discussed and the differences of IGSCC behavior between two-stage and one-stage aged Alloy X-750 are reviewed.

1.4.1 EFFECT OF MICROSTRUCTURE

There are two types of Alloy X-750 used in PWRs, namely the two-stage aged and the one-stage aged materials, designated as AH and HTH, respectively. The former is very susceptible to IGSCC (29), which is
produced by solution treatment, intermediate aging, and a final aging. If the intermediate aging is omitted, it becomes a one-stage aged material. The heat treatment for two-stage and one-stage aging process are summarized in TABLE 1:

<table>
<thead>
<tr>
<th>Material</th>
<th>1-Stage Aged (HTH)</th>
<th>2-Stage Aged (AH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA Temp</td>
<td>980-1150°C, 1-4Hr.</td>
<td>980-1150°C, 1-4Hr</td>
</tr>
<tr>
<td>Int. Age</td>
<td>none</td>
<td>800-870 °C, 24Hr</td>
</tr>
<tr>
<td>Final Age</td>
<td>704°C, 20Hr.</td>
<td>704°C, 20Hr.</td>
</tr>
</tbody>
</table>

The main differences between these two heat treatments come from the distribution, size, and morphology of MC carbides, γ' phase, and M_{23}C_{6} carbides. Among these, grain boundary M_{23}C_{6} carbides are the dominant factor that affects the IGSCC resistance of Alloy X-750.

Research (4,13,30,31) has shown that a high temperature solution treatment dissolves more MC carbide into the matrix than low temperature treatment and eventually supplies more carbon for the subsequent carbide formation. MC carbides usually are TiC carbide, but Nb, Ta, W, and Cr can be partially substituted for Ti. MC carbides are very stable compounds. Forming at temperatures just below freezing, MC carbides are not dissolvable except at very high temperatures. They are generally believed to have little or no effect on the
properties of the material.

Aging at 700-900°C precipitates the γ' particles, primarily in the grain interior. High temperature aging produces larger particles of γ', while low temperature aging forms fine particles. The primary form of the carbide is $M_{23}C_6$, which preferentially precipitates on the grain boundary when the aging is below 850°C (32). Both blocky (globular) and cellular (plate) $M_{23}C_6$ carbides are observed at grain boundary (14,33). They may produce a chromium depleted zone along the grain boundary. But prolonged aging heals the depletion by chromium diffusion from matrix to replenish the zone. Meanwhile, the formation of $M_{23}C_6$ on grain boundary may cause a layer of γ' precipitate free zone (PFZ). A prolonged aging can precipitate fine γ' particles in the previous PFZ (13). The microstructure difference between one-stage and two-stage aged Alloy X-750 can be summarized in TABLE 2:
### TABLE 2  Microstructure of One-Stage and Two-Stage Aged Alloy X-750

<table>
<thead>
<tr>
<th>Material</th>
<th>1-Stage Aged (HTH)</th>
<th>2-Stage Aged (AH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GB Ppt.</td>
<td>$M_{23}C_6$</td>
<td>None or a few, such as Ni$_3$Ti &amp; MC</td>
</tr>
<tr>
<td>$M_{23}C_6$</td>
<td>cellular or globular</td>
<td>N/A</td>
</tr>
<tr>
<td>morphology</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFZ</td>
<td>May or may not exist</td>
<td>Exist after int. age, but eliminated after final age</td>
</tr>
<tr>
<td>Cr Depln. along GB</td>
<td>Severe</td>
<td>None</td>
</tr>
<tr>
<td>IGSCC in PWRs</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Water/Steam</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The main difference between the two heat treatments is the presence/absence of grain boundary $M_{23}C_6$ carbides. Raymond (27) studied the effect of heat treatment on the microstructure and the stress rupture resistance of Alloy X-750. He found that $M_{23}C_6$ carbide was formed perpendicular to the grain boundary by a single low temperature age. This indicates that the carbides were formed by discontinuous precipitation. Rupture testing was done on notch-bar specimen at 649°C and a stress of 80 ksi, and at 732°C with 45 ksi. A two-stage aged material gave better rupture resistance than one-stage aged. Thus two-stage aged X-750 was used extensively in the high temperature application in the aerospace industry. However, the same material used in the PWR environment was not successful. The two-stage aged X-750 was found to be susceptible to IGSCC failures (29).
Yonezawa et al. (13) studied the effects of various heat treatments on IGSCC of Alloy X-750 using U-bend specimen in simulated PWR water at 320, 350, and 360°C. The precipitation of grain boundary $M_{23}C_6$ was examined by TEM with emphasis on the morphology and coherency with the adjacent matrices. They found that for a one-stage aged material, $M_{23}C_6$ precipitates on grain boundaries either discretely or semi-continuously. The semi-continuous $M_{23}C_6$ has type A and type B coherency with the matrix. Type A carbides are coherent with only one side of the matrix, while type B carbides are coherent with both the neighboring matrices in a zigzag configuration. They concluded that the best IGSCC resistance is produced by type B precipitates. Type B chromium carbides are formed by a high temperature solution treatment in the range of 1065-1100°C followed by aging between 704 and 732°C. However, they did not provide mechanistic explanation of why the type B precipitate makes the material more IGSCC resistant.

In addition to the effect of chromium carbides, another main difference between the two heat treated materials is the chromium depletion along the grain boundary. Chromium depletion occurs along the grain boundary in one-stage aged Alloy X-750 and causes the intergranular corrosion in oxidizing environment. Several reporters (14,29,31,34) have confirmed the chromium depletion using Scanning Transmission Electron Microscopy
(STEM). The modified Huey Test (boiling the samples in a 25% nitric acid for 48 hr) also showed signs of intergranular corrosion in one-stage aged materials, but not in two-stage aged samples (29,31). Hosoi et al. (14) attributed the IGSCC of one-stage aged material in 288°C oxygenated water to the chromium depletion zone along grain boundaries. On the other hand, chromium depletion is usually not found in two-stage aged material. Hence the chromium depletion is not the cause to produce the IGSCC of two-stage aged Alloy X-750 in high temperature deaerated water.

It is generally agreed that $M_2\text{C}_5$ carbides form preferentially on the grain boundary in the one-stage aged Alloy X-750, but not form on the grain boundary in the two-stage aged materials (14,31). The presence or absence of grain boundary $M_2\text{C}_5$ carbides is the main difference between the two materials, and may play an important role in the IGSCC of Alloy X-750. The beneficial effect of grain boundary chromium carbide in one-stage aged Alloy X-750 and thermal treated Alloy 600 (Section 1.3) is completely analogous. This implicates that the IGSCC failure in these two materials may be from the same mechanism.
1.4.2 EFFECT OF SEGREGATION

The low solid solubility of nickel base alloys for many elements increases the tendency for grain boundary segregation. Usually segregation of impurity elements such as sulfur, phosphorus, boron, and silicon are detrimental to SCC resistance of the material (4). However, due to the lack of experimental reports, no evidence indicates that impurity segregation has an effect on the IGSCC of Alloy X-750.

Only very few measurements of grain boundary segregation have been reported. Santhanam and Airey (35) found that phosphorus and some sulfur and boron segregated on the grain boundary. However, large variability exists from area to area in the same sample and also from heat to heat. In a study of IGSCC of X-750 in 288°C aerated water, Hosoi et al. (14) used impurity segregation to explain IGSCC of two-stage aged material. On the other hand, Kekkonen and Hanninen (29) attributed the heat-to-heat variability of IGSCC of Alloy X-750 in PWR environment to the segregation of impurities to the grain boundaries. Unfortunately, both reports gave no evidence on the segregation measurement.

Yonezawa et al. (13) detected the segregation of boron, phosphorus, and sulfur to grain boundaries in X-750 given five different heat treatments, including high and low temperature solution treatment in one-stage and two-stage aged specimens. Although those samples have
different IGSCC susceptibility, there is no significant difference in the extent of impurity segregation. Thus they concluded that impurity segregation has no relation to the IGSCC of Alloy X-750.

1.4.3 EFFECT OF STRESS AND STRESS INTENSITY

Stress is necessary to induce the IGSCC of Alloy X-750. Localized plastic deformation may also have a role in the cracking (30). The highly cracked components in service always occupied the most stressed position (3). Other failures were observed at stress concentrators such as threads and discontinuities. Sometimes springs or bolts may receive a stress near their yield point. McIlree (3) suggested that a sustained stress of less than one half of the yielding may be required to totally avoid IGSCC.

Tests for IGSCC using wedge-loaded compact tension (CT) type specimens have been used for the measurement of crack growth rate and the threshold stress intensity factor ($K_{ISC}$). Wilson and Mager (36) measured the IGSCC rates for several different heat treated X-750 samples in 360°C PWR water for up to 6000 hours. Two initial $K_I$ values, 44 MPa√m and 66 MPa√m, were applied to the specimens. For all heat treatments, tests showed crack growth in specimens. Two-stage aged samples showed the fastest growth rate. The crack growth rates were in the range of $10^{-11}$ m/s to $10^{-9}$ m/s, depending on the applied
stress intensity and heat treatment.

Results clearly show that specimens with higher applied loads had faster crack growth rates, which indicates that the IGSCC crack growth was assisted by stress and/or strain in the large plastic zone induced by higher applied load. The remaining stress intensity after 6000 hours exposure ($K_{\text{ISCC}}$) were measured although there was some uncertainty in the rate due to off plane crack growth and crack tunnelling. $K_{\text{ISCC}}$ in two-stage aged specimens was roughly 22 MPa/m or less for both the initial loadings. $K_{\text{ISCC}}$ in one-stage aged was around 37 and 48 MPa/m for initial loading of 44 and 66 MPa/m, respectively. This indicates the $K_{\text{ISCC}}$ of two-stage aged X-750 is lower. Also the crack growth rates of two-stage aged samples were about three times faster than that of one-stage aged. Thus from their experiments, two-stage aged X-750 has been shown to be more susceptible to IGSCC in high temperature PWR water under applied load.

In an earlier paper, Floreen and Nelson (37) studied the effect of heat treatment and composition by measuring the threshold stress intensity $K_{\text{SCC}}$ of Alloy X-750, using wedge-loaded specimens. Experiments were conducted in 360°C water for 2000 hours with pH adjusted to 10 by $\text{NH}_4\text{OH}$. They did not use the subscript I for the expression of threshold stress because the loading was not a valid plane strain condition. Only one-stage aged samples with different aging temperatures and times were
measured. For a standard X-750 composition and one-stage aging, the threshold stress intensity was roughly 50 MPa/m. The results shows that their measurement of IGSCC resistance of one-stage aged samples agrees with that obtained by Wilson and Mager (36) for initial loaded $K$ of 66 MPa/m.

To summarize, IGSCC of Alloy X-750 in high temperature simulated PWR water is assisted by stress and/or strain. Two-stage aged X-750 was demonstrated to be more IGSCC susceptible than one-stage aged samples.

1.4.4 EFFECT OF ADDITION OF ALLOYING ELEMENTS

Alloying element additions may affect the IGSCC resistance of Alloy X-750. Chromium was found to be the most effective (38). Boron was also reported to be beneficial (4). Addition of zirconium may (37) or may not (36) improve the resistance. Phosphorus and sulfur have little or no effect, and carbon, magnesium, nitrogen, lanthanum, cerium have no significant effect (37).

Addition of chromium to Alloy 600 type materials has proved to give superior IGSCC resistance in a primary water environment. Alloy 690 is an example which contains 29% of chromium. Either mill annealed or thermally treated ($700^\circ C$, 15 hours) Alloy 690 showed no failure up to 16000 hours exposure by U-bend test in high temperature primary (39) or hydrogenated water (40).
Donati et al. (38) modified both Alloy 600 and X-750 by adding chromium up to 19% and conducted SCC tests in hydrogenated primary or pure water at 360 and 350°C, and in hydrogenated steam at 400°C. The results show that the higher chromium alloys have much higher IGSCC resistance than the standard alloys, although the modified Alloy X-750 are not immune to cracking. They could not detect any major difference between the standard and high chromium alloys in mechanical properties or microstructure, e.g. size and distribution of intergranular and intragranular precipitates. Hence they argued that the difference in the results of SCC tests might come from the electrochemical properties of the material surfaces. Increasing the chromium content probably raised the resistance of the surface passive oxide film to the environment. This interpretation fits the hydrogen induced void-linkage model (8,9) as well. Since increasing the resistance of the passive oxide film on the surface will inhibit further corrosion or oxidation, the supply of hydrogen will be insufficient and the IGSCC slows down.

Zirconium additions was studied by Floreen and Nelson (37). They found that zirconium could improve the SCC resistance by 50 percent in terms of threshold stress intensity. Zirconium was observed to cause the size of γ' particles uniformly distributed throughout the sample.
Thus they tend to interpret the zirconium effect mechanically. The uniform presence of γ' particles near the grain boundary reduces the localized plastic deformation along grain boundaries. This reduces the tendency of intergranular cracking. Another explanation is that zirconium readily segregates to grain boundaries and ties up or removes deleterious impurities in grain boundaries. Since the effect of segregation is not certain (Section 1.4.2) and there was no difference detected in grain boundary composition after zirconium addition (37), this argument seems not applicable.

In contrast to the report by Floreen and Nelson (37), Wilson and Mager (36) found that the addition of zirconium has no significant effect on the SCC growth in the 360°C PWR water. In another report (4), the beneficial effect of Zr addition is quoted with cautious because of the detrimental effect of Zr in Alloy 600. In summary, from the limited studies the effect of Zr addition is still not well understood.

A number of other alloying element effects were studied by Floreen and Nelson (37), including C, S, Mg, P, N, La, and Ce. It was found that all of them had little or no effect on the stress corrosion resistance.
1.4.5 ELECTROCHEMICAL STUDIES OF THE IGSCC

Electrochemical studies in 340°C primary water show that IGSCC of two-stage aged Alloy X-750 occurs at corrosion potential but not at an oxidizing potential. An oxidizing potential enhances the IGSCC of single aged X-750, which can be explained by chromium depletion along grain boundaries. Galvanic effects between different phases and constituents at crack tip may be important in the IGSCC of Alloy X-750, but the mechanistic process of the IGSCC is still not clear.

In the corrosion process, electrochemistry requires that the total rate of anodic reaction equals the total rate of cathodic reaction so that there is no net accumulation of charge. In stress corrosion studies, one can drive the potential to the anodic side or cathodic side using a potentiostat, or leave it open to the corrosion potential. Examining the cracking behavior at anodic and cathodic potentials enables one to study the controlling process of SCC.

Skeldon and Hurst (30) studied the heat treatment effect on the IGSCC of Alloy X-750 by slow strain rate (SSR) and U-bend testing in 340°C primary water. An external Ag/AgCl reference electrode was used for measurement and control of the potential. The corrosion potential, following one hour exposure to the simulated primary water, was about -670mV (Ag/AgCl). Two strain rates were chosen during the test.
For a strain rate of $1.5 \times 10^{-6} \text{s}^{-1}$, high temperature solution annealed and one-stage aged X-750 were very susceptible to IGSCC at a potential above $-200 \text{mV}$ but no IGSCC occurred below it. Two-stage aged X-750 showed evidence of IGSCC at or close to the corrosion potential. Since a potential of $-200 \text{mV}$ is an oxidizing condition, it is quite possible that the IGSCC of one-stage aged material was caused by the chromium depletion along the grain boundary. The chromium depletion was revealed by the modified Huey tests. U-bend tests of the two-stage aged material also showed it is susceptible to cracking.

The second set of experiment was conducted at a lower strain rate of $2 \times 10^{-7} \text{s}^{-1}$ at corrosion potential in the same environment. Again the one-stage aged material showed no sign of environmentally assisted cracking on the fracture surface consisting with that tested at a higher strain rate. In contrast, the two-stage aged X-750 specimens were prone to IGSCC. The susceptibility was even greater than that at the higher strain rate. This suggests that the initiation of the cracking was slow and a slow strain rate allowed the crack initiation and growth to keep up with the pulling rate. Since the effects of cathodic potential was not studied in their test, the effect of cathodically controlled process such as hydrogen evolution and adsorption can not be assessed.
In the near crack tip region the aqueous environment is determined by local chemical reaction, ingress of species from the bulk, and outgo of species into the outside solution. Because of the high electrical resistivity of bulk solution and the occlude crack tip region, the crack tip potential could be very different from the potential outside the area. Hosoya et al. (41) suggested that hydrogen generation possibly becomes the primary cathodic reaction if acidification occurs inside the crack tip region. They proposed that local galvanic effects may result in accelerated cracking process. The electrochemistry of several alloys was studied which simulates different phases/constituent at/or near the grain boundary. Fig. 1 is a schematic representation of the phases or constituent existing at a grain boundary crack tip. Those phases can be combined to form a number of galvanic cells, including:
- precipitates/local bare surface
- precipitate/grain boundary
- precipitate/passive crack flanks
- local bare surface/passive crack flanks

In their measurements, several alloys were examined, each representing the base matrix, chromium depleted matrices, and several different compositions of \( \gamma' \) phases. Tests were conducted in the neutral and acidic (pH=3) solutions to simulate the possible acidification condition. They observed that:
Figure 1. Schematic presentation of tip of a propagating stress corrosion crack tip in a precipitation-hardened alloy. Local Galvanic cells are illustrated (41).
1. In anodic polarization measurement, low chromium alloy has the highest current density.
2. At 93°C, the free corrosion potential of Ni₃Al (γ') is very different from that of X-750 matrix. But the difference is smaller at 288°C.
3. The hydrogen exchange current density of Ni₃Al at 93°C is much higher than that of the matrix.
4. Galvanic coupling of γ' alloy and matrix at 93°C may result in a significant corrosion current, where the γ' acts as the anode and the matrix as the cathode.
5. M₂₃C₆ carbides are cathodic relative to the matrix.

It is concluded that at temperature around 100°C, a two-stage aged X-750 has an acceleration of crack growth rate in high purity water due to the high corrosion current of the γ'-matrix couple at the crack tip. They proposed that hydrogen cracking was the mechanism because the couple could provide an extremely localized source of hydrogen at the crack tip. For temperature up to near 300°C, the γ' may still be more active than the matrix but the difference is smaller and the generation of hydrogen is less. Thus stress corrosion cracking was proposed for the IGSCC mechanism at high temperatures. However, the small anodic area and some possible polarization inside the crack tip region may still cause the γ' to dissolve and generate hydrogen, thus hydrogen cracking can not be excluded in tests at 300°C.
On the other hand, the IGSCC resistance of a single aged material can be interpreted by galvanic effects as well. $M_{23}C_6$ carbides always form on the grain boundary which is cathodic to the matrix. With a large anode/cathode ratio, only small amount of hydrogen can be generated. Hence the cracking of single aged X-750 is more difficult due to the lack of hydrogen at the crack tip region.

The research of Hosoya et al. (41) offers good insight into what is occurring electrochemically during the IGSCC of X-750 in the high temperature water. Although they have explained the microstructure factors on the IGSCC in terms of galvanic effects, however, the atomistic mechanism of the IGSCC is still not clear.

1.5 VOID-LINKAGE MODEL FOR THE IGSCC IN HIGH TEMPERATURE PRIMARY OR DEAERATED WATER

A hydrogen induced void-linkage model proposed by Shewmon (8) can explain the characteristics of the IGSCC of Alloy 600 as discussed earlier in section 1.2. The mechanism was further analyzed experimentally by Shen (9) and Shen and Shewmon (42). Fig.2 shows schematically the proposed model for IGSCC in high temperature water/steam system. Shewmon (8) suggested that the IGSCC is aided by the nucleation and growth of a fine array of grain boundary microvoids in front of an advancing crack. Nucleation of the voids is aided by high pressure of
Figure 2. Schematic presentation of void-linkage model for hydrogen induced IGSCC. (9)
methane, which can be formed through reaction of hydrogen generated near the crack tip and carbon supersaturated in solution as a result of heat treatment. The stress and methane pressure drive the growth of voids and finally voids join to form fissures. Thus this type of failure is always along grain boundaries.

The hydrogen comes from the reaction of $\text{H}_2\text{O}$ with clean metal surfaces, and the fugacity of hydrogen can be extremely high locally at the root of the crack (42). Hydrogen will diffuse from this region into the rest of the sample. Thus the bubble nucleation only occurs near the crack tip where the hydrogen concentration is the highest. In order to nucleate bubbles and grow the crack deeper, the bubbles must grow to link up and move the hydrogen source into the sample.

There are two major ways that assist the nucleation of microvoids, including methane pressure and the applied stress. The nucleation of microvoid can be further aided by the impingement of slip lines at the grain boundary as demonstrated by Lim and Raj (43) by low-cycle fatigue of nickel at intermediate temperature. Shewmon (8) has shown the combination of the methane pressure and applied stress could give homogeneous nucleation of bubbles along the grain boundary. The formation of methane bubbles requires carbon in solution near the grain boundary. In a microstructure with grain boundary carbides, the carbon activity at grain boundary is low and the nucleation of
methane is very difficult. Thus the IGSCC is usually not observed in a microstructure with plenty of grain boundary chromium carbides. For a microstructure without intergranular chromium carbides, the initial carbon activity is high, thus methane bubbles can be nucleated.

At the start of the growth stage, the high pressure methane and the applied stress drive atoms away from the void surface by diffusion thus allowing the methane to expand and do work. Due to the relatively low testing temperature, such diffusion process occurs more rapidly along the grain boundary. Once voids start to grow, the matrix will rapidly drain its carbon due to slow carbon diffusion. Thus the supply of carbon is insufficient and the methane pressure drops rapidly. Since there is not enough methane pressure inside the voids, the growth of voids is mainly from the assistance of applied stress.

Using an equation originally derived by Raj and Ashby (44) and later modified by Raj et al. (45) for grain boundary cavity growth at elevated temperature, Shewmon (8) was able to model the growth of the IGSCC of Alloy 600 in high temperature deaerated water. The time for an array of grain boundary bubbles of spacing 2b to grow by grain boundary diffusion to link up can be given by the equation: (45)

\[ t_f = \frac{0.012 kT (2b)^3 h(\theta)}{D_b \delta \Omega (P+\sigma_n)} \] 

(1.1)
Where $D_b$ is the grain boundary self diffusion coefficient, $\delta$ the boundary thickness, $\Omega$ the atomic volume, $P$ the internal gas pressure, $\sigma_n$ the remote applied tensile stress normal to the grain boundary, and $k$ is the Boltzmann constant, $T$ the absolute temperature. $h(\theta)$ is the shape function which reflects the decrease in bubble volume that accompanies a decrease in $\theta$ with fixed $r$. Bubble spacings can be estimated by inserting numbers for each parameters in equation (1.1). For Alloy 600 underwent IGSCC in 350°C water, Shen and Shewmon (42) estimated that the bubble spacing would be 0.5 to 0.2 μm. The most important experimental observation was two-stage replica TEM studies, which can be used to check the validity of the model. They clearly showed that discrete microvoids nucleated on the grain boundary near the main crack. They then grow into a more dense, unresolvable, set of bubbles or cracks, closer to the crack. The spacing of the discrete bubbles farthest from the main crack is about 0.2μm, which is consistent with the estimation by equation (1.1). Another worth noting point is that discrete bubbles were observed only in a distance of two grain diameter from the crack. This indicates the nucleation of methane bubbles only occurs very near the source of hydrogen where fresh metal surface is exposed to react with water.
In addition, Shewmon et al. (46) studied hydrogen trapping and methane formation in Alloy 600 which underwent stress corrosion cracking in simulated primary water at 350°C. Measuring the release of hydrogen by heating specimens at constant rate, they found there was negligible amount of methane present in the IGSCC sample after fracture. However, hydrogen was found in the specimen in forms of being dissolved in the lattice and trapped in deeper traps. Those traps were believed to be internal surfaces or pores. Hydrogen is trapped due to chemisorption which further decreases the surface energy of the crack and the angle between the bubble surface and the grain boundary. Thus during the crack growth, the shape of the crack-tips is modified to be crack-like (42), i.e. more elongated along the grain boundary rather than spherical.

1.6 IGSCC OF 410SS IN PRIMARY OR DEAERATED WATER

410SS is a martensitic stainless steel, containing 0.15 % carbon and 11.5 - 13.5% chromium. 410SS is used in a quenched and tempered form, which is a structure of tempered martensite. In the PWR environment, IGSCC has been observed in components which were improperly tempered at low temperatures, with a hardness higher than $R_c$ 26 (47).
Tempering of 410SS at low temperatures produces Cr₇C₃ carbides in the matrix, retains high strength in the martensite, and causes temper embrittlement. These factors could affect the 410SS susceptibility to the IGSCC in PWR environment, which are discussed in the following sections.

1.6.1 MICROSTRUCTURE OF 410SS AFTER TEMPER

Increasing the tempering temperature of 410SS produces different carbides in the microstructure. A temper at 500°C or above precipitates more Cr₂₃C₆ carbides on the grain boundary.

Quenching 410SS from solution temperature (980°C) transforms austenite to martensite, and forces carbon to supersaturate in the matrix. The following temper treatment forms carbides in the solution. Irvine et al. (48) studied a 0.1%C-12%Cr steel and reported that after tempering at 300°C, Fe₃C particles formed, and the hardness decreased. A temper in the range between 400 and 450°C produced secondary hardening, which was attributed to the precipitation of fine Cr₇C₃ carbides in the matrix. Tempering at higher temperatures (49) or for longer times at 500°C (48), Cr₂₃C₆ carbides formed at the expense of Cr₇C₃ carbides in an over-aging process. Cr₂₃C₆ carbides were found to form predominantly at prior austenite grain boundaries or martensite plate. Kuo (50,51) observed similar results in high chromium steels using X-ray powder
method to identify these two types of carbides. Hence the main difference on the grain boundary for tempering at different temperatures is the distribution of chromium carbides. A temper at 500°C and above produces grain boundary Cr$_2$C$_6$ carbides, while tempering at lower temperatures the grain boundary is free of chromium carbides.

1.6.2 EFFECTS OF STRENGTH

IGSCC of 410SS occurs in a high strength structure, which indicates the material could receive higher stresses from loading, and hydrogen might have an important role in the cracking process.

Tempering at different temperatures produces various strength of 410SS. Tempering treatment at low temperatures gives high strength materials, while a high temperature temper softens it. Tempering up to 500°C retains high hardness (strength) of the alloy, due to secondary hardening effects from the precipitation of Cr$_7$C$_3$ carbides (48,52). Since a high strength steel is more resistant to the plastic deformation, under an applied load, the steel receives higher stresses without yielding.

IGSCC in high strength 410SS occurs in PWR environment, which is indicated by a hardness higher than $R_C$ 26 (5). The high strength of 410SS affects the IGSCC in two folds. First, the material receives higher stress
under a load without yielding. Since IGSCC is stress assisted, high applied stress accelerates the IGSCC. Tempering at 500°C or below does not drastically decrease the hardness of 410SS, and the material receives high stresses on loading. Thus, in PWR environment, IGSCC susceptibility of this material increases. Secondly, a higher strength might increase the tendency to hydrogen embrittlement, which is generally observed in high strength steels (53,54). In addition, many authors tend to accept hydrogen embrittlement as the cracking mechanism for stress corrosion cracking of high strength 12-13%Cr martensitic stainless steel tested in 3% NaCl solution at room temperature (55). In the present case, the high strength 410SS is susceptible to IGSCC in the PWR environment. Thus IGSCC could be enhanced by hydrogen, and the high strength of the steel further assists the cracking.

1.6.3 TEMPER EMBRITTLEMENT OF 410SS

IGSCC of 410 stainless steel in high temperature deaerated water occurred by a low temperature temper, while a high temperature temper decreases the IGSCC susceptibility of the steel (5). IGSCC of 410SS could be related to the temper embrittlement phenomenon of 12%Cr steel tempered in the range of 400-600°C. Both transgranular and intergranular fracture were observed in the embrittled fracture surface. There are a number of
mechanisms proposed to explain the embrittlement, including secondary hardening effect by chromium carbides (48,56) for the transgranular embrittlement, grain boundary Cr$_{23}$C$_6$ carbides (57,58) and impurity segregation (59) and for the intergranular cracking. In addition, plastic zone size (57) was proposed to determine the fracture mode. Since the IGSCC of 410SS occurs along grain boundaries, impurity segregation and Cr$_{23}$C$_6$ carbides could have a major role in the cracking.

1.6.3.1 Transgranular Temper Embrittlement

Studying transgranular temper embrittlement, Irvine et al. (48) and Banerjee et al. (56) proposed that secondary hardening effect by chromium carbides in the matrix was the prime cause for embrittlement.

Irvine et al. (48) tested the effects of increasing the tempering temperature on the impact properties of 12%Cr steels at room temperature. They observed that impact absorbing energy drops until it reached a minimum by tempering at 550°C. They suggested that due to the secondary hardening effects in this temperature range, the resistance of grains to plastic deformation increases, thus the grain interior became intrinsically brittle. Moreover, when the grain boundary chromium carbides becomes coarser, some local carbon and alloying elements may be locally depleted. They proposed that the overaged grain boundary carbides lead to the crack initiation and
the crack propagates in the less crack resistant grains in
a brittle manner.

In another report, Banerjee et al. (56) studied a
martensitic stainless steel similar to 410SS except with
some additions of Mo, W, and V. They measured notch
properties using fatigue pre-cracked tensile specimens.
Toughness was calculated by the shear percentage on the
fracture surface. A drop in toughness was observed with a
minimum occurred by tempering at 510°C. At the minimum
toughness, a flat transverse fracture was found, with
cleavage steps on the fracture facets. They examined the
sample in TEM and observed that M₃C carbides were
dissolved by tempering between 480 and 540°C and Cr₂₃C₆
carbides were formed at dislocation jogs and
intersections. Since M₃C carbides softens the martensite
and improves the toughness (48,56), the elimination of the
M₃C carbides could decrease the toughness. Secondly, they
observed that the precipitation of Cr₂₃C₆ carbides have a
locking effect on the motion of the dislocations, and thus
increases the brittleness of the matrix. However, their
observation of secondary hardening by M₂₃C₆ carbides
differs from other reports. A number of authors (48,52)
suggested that the hardening is induced by M₇C₃ instead of
M₂₃C₆ carbides.

Since IGSCC of 410SS occurs along grain boundaries,
transgranular fracture mechanisms proposed by Irvine et
al. (48) and Banerjee et al. (56) could not explain the
cracking process. To explain the IGSCC of 410SS, possible mechanisms used to explain the intergranular embrittlement of 12%Cr steels will be reviewed in the next section.

1.6.3.2 Intergranular Temper Embrittlement

Temper embrittlement of martensitic steel sometimes occurs along the grain boundary. Berry and Brook (57) demonstrated a small plastic zone leads to intergranular cracking. They attributed grain boundary Cr$_2$3C$_6$ carbides to be a weakening agent to the grain boundary. Impurity segregation to the grain boundary is another factor that may induces the embrittlement. Lemble et al. (59) observed the effect of phosphorus on the embrittlement of 12%Cr martensitic steels.

Berry and Brook (57) proposed that plastic zone size determined the fracture mode of the cracking. A small plastic zone size induces intergranular fracture, which is further assisted by the grain boundary weakening agent of Cr$_2$3C$_6$ carbides. Berry and Brook (57) studied the tempering embrittlement of a 0.2%C and 12%Cr steel using fracture toughness experiments. They reported a temper at 540°C produced a toughness minimum, while tempering at 600°C and above improved the toughness. They found that the fracture mode was close related to the plastic zone size (p.z.s.). The largest p.z.s. resulted in dimple rupture, a intermediate p.z.s. caused quasi-cleavage mode, while the smallest p.z.s. associated with intergranular
fracture. In their experiments, the most severest embrittlement was intergranular fracture produced by a tempering at 540°C. In addition to the small p.z.s., they also considered grain boundary \( \text{Cr}_2\text{C}_6 \) carbides to be a weakening agent because the carbides precipitation and intergranular fracture occurred simultaneously by a tempering at or above 500°C. However, they did not explain how the plastic zone size and the chromium carbides assisted the intergranular fracture. Moreover, grain boundary \( \text{Cr}_2\text{C}_6 \) carbides were observed to continuously form at higher temperatures up to 700°C (48,50). If \( \text{Cr}_2\text{C}_6 \) carbides did cause the intergranular fracture, the maximum toughness of tempering at 600°C in their report is difficult to explain.

In addition to the arguments on the chromium carbide formation, another possibility is the reversible temper embrittlement, causing by impurity segregation to the grain boundary (60,61). Tempering in the range between 375 and 650°C segregates impurities, such as P, Sb, Sn, and As to the grain boundary. They weaken the grain boundary and cause the intergranular fracture.

IGSCC of 410SS occurs by a tempering at a same temperature range that also causes the temper embrittlement. Thus these two cracking phenomena might be related. Lemble et al. (59) studied phosphorus additions and the segregation kinetics on the room-temperature impact properties of 12%Cr martensitic steels. They found
that the minimum in impact toughness occurred at 550°C temper for a steel with 250 ppm phosphorus addition by a brittle intergranular fracture. Using Auger electron spectroscopy, they concluded that the intergranular embrittlement was caused by simultaneous segregation of P, Ni and Cr to the former austenitic grain boundaries. Whereas the steel without high phosphorus additions showed cleavage fracture at the toughness minimum, which was believed to be associated with the Cr$_7$C$_3$ precipitation in the matrix. Thus it is reasonable to believe that impurities segregate to the grain boundaries during tempering at temperature between 400 and 550°C will reduce the IGSCC resistance of the 410SS.

Berry and Brook (58) measured the toughness of a 12%Cr martensitic stainless steel by three-point bend specimens. They observed a fall in toughness with increasing the time of the embrittlement treatment at 550°C. This indicated that the impurity segregation to the grain boundary may become an important factor to the embrittlement, though not mentioned in their report. They also noticed that even in the absence of an embrittlement treatment, the specimen still showed an intergranular fracture in toughness tests below room temperature. All the specimens were tempered at 680°C before test, and M$_{23}$C$_6$ carbides were formed on the grain boundary. Thus they attributed the grain boundary embrittlement to those grain boundary chromium rich carbides.
In summary, the IGSCC of 410SS in high temperature water may relate to the room temper embrittlement of the material. The combination of impurity segregation to the grain boundary, hydrogen embrittlement, and grain boundary chromium carbide may contribute to the IGSCC.

It was shown that the hydrogen induced void-linkage model is in good agreement with the characteristics of Alloy 600. But the nucleation of the bubbles and the stress effect on the growth of voids are still not well studied. The IGSCC of Alloy X-750 are very similar to Alloy 600, the validity of this model will be checked for Alloy X-750. On the other hand, IGSCC of 410SS is not well understood, which could stem from other mechanisms.

In the course of this thesis, five sets of experiments were designed to study:
1. the nucleation of grain boundary bubbles in Alloy 600
2. the crack growth of IGSCC in Alloy 600
3. the validity of hydrogen induced void-linkage model for IGSCC in Alloy X-750
4. the crack growth of IGSCC in Alloy X-750
5. the cracking mechanism of IGSCC in 410 stainless steel
CHAPTER II

EXPERIMENTAL PROCEDURES

2.1 ALLOY 600

2.1.1 STUDY OF GRAIN BOUNDARY BUBBLES

To study the nucleation of grain boundary bubbles, Alloy 600 U-bend samples was tested in high temperature steam to generate IGSCC, then a TEM two-stage replica technique was used to examine the size and distribution of bubbles. Reverse U-bend (RUB) specimens were used because the stress state of RUBs resembles the U-bend region in a PWR steam generator where IGSCC frequently occurs (2). The fractured specimens were then cut and polished for replicating the grain boundary cracks. The two-stage replica technique was chosen because of its high resolution for sub-micron structures and large area of the specimen that could be examined.

2.1.1.1 Materials and Test Specimens

RUB specimens was made from Alloy 600 tube, with an outside diameter of 22.2 mm and a wall thickness of 1.27 mm. The tube was supplied by Babcock and Wilcox.

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Corporation in the mill annealed condition, that is it was annealed at approximately 930°C and cooled at a rate of 256°C/min. The chemical composition and the mechanical properties at room temperature are shown in TABLE 3.

<table>
<thead>
<tr>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>C</th>
<th>S</th>
<th>Si</th>
<th>Mn</th>
<th>Cu</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>75.0</td>
<td>15.8</td>
<td>8.04</td>
<td>0.038</td>
<td>0.002</td>
<td>0.32</td>
<td>0.26</td>
<td>0.01</td>
<td>0.022</td>
</tr>
</tbody>
</table>

TABLE 3. Chemical Composition (wt%) of RUB Specimens and Mechanical Properties at 25°C

<table>
<thead>
<tr>
<th>YS</th>
<th>UTS</th>
<th>Elon. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>389 MPa</td>
<td>737 MPa</td>
<td>37</td>
</tr>
</tbody>
</table>

The microstructure of the mill annealed tube consists of chromium carbides inside the grain and clean grain boundaries. Such a microstructure has been proven to be IGSCC susceptible in the high temperature deaerated water and steam (17). Figure 3 gives the microstructure of the material, which was etched in 5% Nital solution at 4 volts for 7 to 10 seconds.

RUB specimens were prepared by Metals Samples Co., Inc. The procedure included cutting the tube to 10 cm long, slitting it in half, and reverse bending around a mandrel to a U-shape such that the interior of the tube was facing out. A 316 stainless steel bolt and nut were used to tighten two legs of the U-bend to exert a load on the specimen. The separation of the two nearest sides of the straight legs was 2.54 mm apart. The shape and dimension of the RUB specimens are shown in Figure 4. No further heat treatment was used and the specimens were
Figure 3. Microstructure of annealed Alloy 600 tube specimens. Electrolytic etch in 5% Nital solution. (a) 400x (b) 1000x.
Figure 4. Reverse U-bend specimens used in the present study.
degreased by acetone in an ultrasonic cleaner for two minutes before putting the specimens into the pressure vessel.

2.1.1.2 Preparation of IGSCC in RUB specimens

A 316 stainless steel pressure vessel with a capacity of 300 cc was used for the test. It was manufactured by High Pressure Equipment Co. The heating source for the vessel was a specially made furnace open at only one end and using Lindberg 1000°C electric heating units - Model 50311, Type 86-SP. Temperature was controlled by a Weather-Measure temperature controller - Model TPC-1. A schematic drawing of the set up of the autoclave is shown in Figure 5.

To obtain IGSCC in Alloy 600 specimens, conditions suggested by Shen (9) was used, which would generate the cracking in 400 hours. The testing environment was deaerated steam at 380°C with 0.1 MPa (STP) hydrogen overpressure. Deaeration was done starting with demineralized distilled water and purging with argon gas for at least 24 hours. Then 36g of water was transferred immediately into the autoclave, the air evacuated by a mechanical pump and the vessel backfilled with hydrogen. Evacuation and backfilling were repeated three times to make sure the environment inside the vessel was free of oxygen. Finally, a partial pressure of pre-purified hydrogen at 0.1 MPa was introduced into autoclave then the
Figure 5. Schematic diagram of the high pressure vessel for reverse U-bend testing. (9)
vessel was closed. Thus the experiment was done in a stagnant solution. The autoclave was heated up to 380°C and held there. The 36g water gave a superheated steam with a pressure at about 20 MPa according to the Steam Tables (62). Every three or four days the furnace was turned off, the sample cooled for three hours, and the autoclave was opened to check for cracks in the RUBs. If no cracks were found, the testing was continued until the IGSCC was observed.

2.1.1.3 Two-Stage Replica Technique

Fractured RUB specimens were cut into 1.5 cm by 1.5 cm pieces. Then the a flat surface in the cracked areas of the specimen was polished on silicon carbide papers through grit 400. Final polishing was done by alumina powders of 0.3μm and 0.05μm on water wetted polishing cloth (Microcloth, made by Buehler Ltd).

Figure 6 shows the steps involved in the preparation of two-stage replicas. First the specimen was wetted with one drop of acetone. The specimen was set nearly horizontal to let excess acetone flow away but not let one side of the specimen dry off much quicker than the other. Just before the acetone dried off (about 2 sec before), replicating tape was placed on the specimen surface using small tweezers. The replicating tape was 0.022mm thick (Acetyl Cellulose film) manufactured by Ernest Fullman, Inc. One had to wait for at least two minutes for the
Figure 6. Schematic representation of the steps involved in making two-stage replicas.
tape to completely dry. Then the tape was peeled from the specimen. These steps were repeated at least three times to make sure the sample was cleaned. Finally, the replicating tape was adhered on a glass slide with imprinted side up.

Next two steps were shadowing and carbon deposition for the replica. The replica was put into a vacuum deposition system manufactured by Edward Co., and was evacuated to a pressure of $10^{-4}$ to $10^{-5}$ torr. Shadowing was done using a platinum-carbon pellet positioned at an angle of $20^\circ$ with the sample surface. The shadowing pellets were purchased from LADD Co. The replica was then coated with carbon from the top to give mechanical strength to the film. Finally, the area of interest was cut with a pair of scissors into a 3mm x 3mm square, and placed on a copper grid. The copper grid was inserted into a condensation washer, purchased from Ernest Fullman, Inc., in which the plastic tape was dissolved and removed by refluxing acetone vapor. After the unit was cooled, the copper grid with its thin layer of replica carbon film was ready for TEM observation.

2.1.2 STUDY OF THE EFFECTS OF SLIP LINE IMPINGEMENT AT GRAIN BOUNDARIES

For examining the effect of slip line impingement on the grain boundary on the microvoid nucleation, a specimen was bent at room temperature. The bend area was examined
in TEM using two-stage replica technique.

The specimen was cut from an Alloy 600 plate (1.5 cm thick) supplied by INCO Alloys International, Inc. Although the exact heat treatment was not known, the plate was assumed to be an as rolled plate. The microstructure of the as received material is shown in Figure 7a and 7b. The microstructure shows a duplex distribution of grain size, with small grains around 15μm in diameter and large elongated grain of 75μm in length. The chemical composition of the plate material is listed in TABLE 4:

<table>
<thead>
<tr>
<th>Material</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>C</th>
<th>S</th>
<th>Si</th>
<th>Mn</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>77.66</td>
<td>14.64</td>
<td>6.96</td>
<td>0.06</td>
<td>0.001</td>
<td>0.15</td>
<td>0.28</td>
<td>0.25</td>
</tr>
</tbody>
</table>

A strip with dimension of 10cm x 1.5cm x 1.5mm was cut from the Alloy 600 plate. Then the surface of the specimen was polished through 400 grit silicon carbide polishing paper. A layer of lacquer was painted on the sample surface except that a window of 1.2cm x 1.2cm was left open for electro-polishing.

Electro-polishing was used because it offered a high quality of smooth surface so that ultrafine slip lines would show up easily after deformation. The electrolyte for the polishing was 1 part (by volume) perchloric acid (70% concentrated) in 9 parts methyl alcohol.
Figure 7. Micrographs of as received Alloy 600 plate material. Electrolytic etch in 5% Nital solution. (a) 400x (b)1000x.
The electrolyte was put into a beaker, which was then cooled to -50°C by liquid nitrogen. A circular stainless steel sheet was made as cathode, and the sample as anode. A potential of 20 to 30 volts was applied for 1 minutes. After polishing, the specimen was taken out immediately and immersed in a methyl alcohol bath, then wash with distilled water and methyl alcohol in an ultrasonic cleaner. The sample was inspected under optical microscope. A satisfactory sample showed smooth and shining surface with no pits on the surface.

The sample was bent around a 1.25 inch (3.175 cm) diameter steel bar until the angle between the two legs reached 135°. Then two-stage replica technique described in section 2.1.1.3 was used to replicate the deformed region. A JOEL 200CX was used for observation, with an accelerating voltage of 100kV.

2.1.3 STUDY OF THE EFFECTS OF STRESS INTENSITY AND TEMPERATURE ON THE IGSCC CRACK GROWTH RATES

The linear-elastic fracture-mechanics (LEFM) approach to stress corrosion cracking testing was initiated by Brown et al. (63). Novak and Rolfe (64) developed the Modified Wedge Opening Loaded (MWOL) specimen to study crack growth of a fatigue pre-cracked sample undergoing stress corrosion cracking. The MWOL is a constant crack-opening-displlt (COD) specimen loaded by a bolt and loading tup. It is a $K_I$-decreasing specimen, since as the crack
grows the stress decreases more than the compensation from the increase of the crack length. In the present study, the effects of stress intensity and temperature on the crack growth rate were studied using MWOL specimens. The DC-potential drop technique (65), which has been proven to be very accurate in the crack length measurement (66), was used to monitor the crack length. The potential difference from the sample was measured by a digital voltmeter interfaced with a personal computer. After collection of the data, the specimen was fractured to study the fracture surface.

2.1.3.1 Material

The material used for crack growth studies was the same as the plate used in the slip lines study. Small blocks (2" x 1.5" x 0.5") were cut from the plate, sealed in evacuated quartz tube, annealed at 930°C for 10 minutes, and air cooled to room temperature. This heat treatment was to insure that the microstructure was susceptible to the IGSCC cracking. At room temperature, the yield strength was 305 MPa, tensile strength was 713 MPa, and the elongation was 52% for a 10 mm gauge length. Micrographs of the specimens are shown in Figure 8. The microstructures show that most of the chromium carbides were intragranular carbides, and the grain size was around 25μm.
Figure 8. Micrographs of annealed Alloy 600 plate used for MWOL specimens. Electrolytic etch in 5% Nital solution. (a)400x (b)1000x.
2.1.3.2 MWOL Specimens

The heat treated specimen blocks were machined into MWOL specimens. Figure 9 shows the crack plane orientation code for rectangular sections in the ASTM Standard E-399 for plane-strain fracture toughness measurement (67). In the present test, T-L specimens were used, which had a fracture plane whose normal was in the transverse direction of a plate and the crack propagation direction followed the longitudinal direction of the plate. Figure 10 shows the detailed machine drawing for a MWOL specimen. Due to the size limit of the testing instrument, the specimen was a 1/2 T specimen (0.5 inch or 1.27 cm thick). Side grooves were machined on each side of the specimen. Those grooves could reduce the plain stress condition which would generate shear lips there, and prevent out-plane cracks.

The loading bolt and tup are shown in Figure 11. They were made by Alloy 718 (53Ni-19Cr-19Fe-5Nb-3Mo-1Ti) for good resistance to corrosion and high temperature deformation. They were machined from an Alloy 718 rod, and then were heat treated in two-stages to give high strength. The heat treatment procedures were taken from the Metals Handbook (68). These included a solution anneal at 980°C for one hour and air cool, followed by treatment at 720°C for 8 hours, furnace cooling to 620°C and holding for total of 18 hours, and finally air cooled to room temperature. The hardness after this heat
Figure 9. Crack plane orientation code for rectangular sections (67).
Figure 10. Detailed machine drawing for the MWOL specimen. (64)
Figure 11. Detailed machine drawing for the loading bolt, tup and insulating disc. (9)
treatment was $R_C$ 45.

A zirconium alloy disc (Zr-705) was used for electrical insulation between the bolt and tup. A rod of Zr-705 was annealed at 1038°C for 15 minutes and water quenched to $R_C$ 28, then 1.27 mm (0.05") thick discs were cut and oxidized in air at 500°C for 24 hours to grow a layer of oxide to give electrical insulation.

2.1.3.3 Fatigue Pre-Crack and Loading

Fatigue pre-cracking was used because this avoided the difficulties that might be involved in crack initiation. The procedure followed the ASTM recommended practice E-399 (67). The fatigue was done on a servo-hydraulic machine (Instron 1331) in a tension-tension mode from 260 lbf to 2600 lbf. The loading was in a sine function mode and the fatigue frequency was 5 Hz. Usually one obtained a fatigue crack 2 to 4 mm long in 10000 to 20000 cycles.

Loading of the MWOL sample was carried out by measuring the back-face strain of the specimen while tightening the bolt. The back-face is defined as the face opposite to the side with the crack opening. Deans and Richards (69) developed a sensitive method to monitor the loading by measuring the back face strain of the specimen. Appendix A gives the details of their method and the calibration table. Since the loading on the front was tension, the stress on the back face would be compressive.
After the fatigue pre-crack was made, a measuring microscope was used to measure the crack length. Using the crack length and a load, one can calculate the stress intensity factor. An equation from Lisagor (70) was used to determine the $K_I$ for WOL specimens, and the calculation is given in Appendix B. Thus one could calculate what load will be needed for a specific $K_I$ for that crack length. The desired compressive strain (determined by the load) for that $K_I$ was calculated from Appendix A. The loading procedures are shown in the following steps (9):

1. Bond a strain gage to the centre of the back face of the pre-cracked specimen parallel to the loading direction. The gage was manufactured by Measurement Group, Inc., the model was EA-06-125AC-350-LE. Caution should be made during the handling and installation of the gage. A small bending will destroy the gage.

2. Place the bolt, tup, and disc onto the specimen.

3. Grip the specimen in a vise and tighten the bolt to the desired strain using a torque wrench. The strain was measured by a strain gage conditioner/amplifier (Measurement Group, Inc., Model 2100 system).

4. Take the specimen out of the vise, remove the strain gage, and degrease the specimen in an ultrasonic cleaner with acetone. The specimen is then ready to be tested.
In the present study, an initial $K_I$ of 60 MPa/m was applied. This was to be compared to the data of Shen who used an $K_I$ equal to 80 MPa/m (9).

2.1.3.4 DC Potential Drop Technique

Since the present testing condition involved a high temperature, high pressure water/steam system, the crack growth measurement had to be made inside the autoclave. To cope with this requirement, a direct current (dc) electrical potential drop method (71) was used, which gave accurate measurement in the aggressive environment. The method included flowing a constant current through the specimen and measurement the potential difference across the two sides of the crack. As the crack grew, the net cross section decreased. Thus the electrical resistance increased and so did the potential. Monitoring the potential difference during the test run, one could convert it to the crack length. Conversion of potential to crack length was done by a method developed by Klintworth (72), using finite element potential - crack length calibrations. Details of the conversion are included in Appendix C.

2.1.3.5 Experimental Apparatus

A schematic drawing of the testing apparatus is shown in Figure 12. The autoclave was the same as described in Section 2.1.1.2, however, the design of the lid was
different. Besides the one for thermocouples, there were two more outlets, one for input of constant current and one for the output of the potential signal.

A highly stable constant current of 4 amperes (supplied by a Sorenson Power Source Model XTS 7-6) was pass through the specimen. The current leads to the specimen were 0.76mm diameter platinum wires in order to minimize the resistive heating. A switched dc technique was used to eliminate the thermocouple effect due to the junction of dissimilar metals. The polarity of current was switched after each potential measurement using a switch made of two pairs of solid state relays which were controlled by the parallel port in an IBM-PC. The same technique was used by Shen (9) and the details were described in Reference 9.

Four 304 stainless steel wires, 0.5 mm in diameter, were used for the potential leads. Figure 13 shows the locations of those potential leads along with the current leads on the specimen. Pair 3 was the probe which gave the front face potential measurement. Pair 2 was another pair of potential leads near the back of the specimen which was used as reference probes for temperature correction. All the leads were tightened to the specimen surface by 316 stainless steel bolts. Each time before tightening, the sample surface and the leads were sanded and cleaned with acetone to assure good contact. All wires were covered with alumina (99.8% pure) or zirconia
Figure 12. Schematic drawing for the apparatus used in the crack growth rate measurement. (9)
1: Current Leads
2: Reference Probes
3: Potential Probes

Figure 13. Location of Potential Leads and Current Leads on the MWOL Specimens.
tubes to provide electrical insulation in high temperature water.

The front face potential was measured by a digital voltmeter, Fluke Model 8842A, which has a resolution of 100 nV with capability (IEEE interface) for interfacing to a personal computer. Temperature was measured with another digital voltmeters, Keithley Model 197, with a resolution of 1µV. An interface card, made by National Instruments - Model GPIB-PC2A, connected all three signals to an IBM-PC-XT computer. A control code written in QuickBasic was used for data acquisition (9), which controlled the reverse of the polarity of the current, trigger of voltmeters, collection of potential differences and time elapsed. In the present study, each data point included an average of 100 measuring cycles. During the test, the standard deviation of the measurement was calculated. Typically, a deviation of less than 1µV was recorded out of a potential drop of 170µV. The collection of data continued until the final potential measurement exceeded the initial value by at least 3 times of the magnitude of the standard deviation. Verification of agreement between real crack length and that indicated by the potential measurement was done and reported elsewhere (9), and the agreement was good.
2.1.3.6 Test Conditions

The tests were performed in a deaerated pure water/steam stagnant system, in which 36g water and 0.1 MPa hydrogen was added at room temperature. Four different temperatures were chosen for the test, 320, 340, 360, and 380°C. Water becomes superheated steam at these temperatures. The pressure of the steam was not measured in order to avoid condensation of steam in the tubing system. According to the Steam Tables (62), the steam pressures for 320°C, 340°C, and 360°C were 11.3 MPa, 14.6 MPa, and 18.6 MPa, respectively. After all the experiments, the specimen was fatigued in the tension-tension mode to open up the fracture surface. Finally, the fracture surface was examined by SEM.

2.2 ALLOY X-750

2.2.1 STUDY OF IGSCC OF ALLOY X-750 BY U-BEND SPECIMENS

U-bend specimens were used to study the IGSCC susceptibility of Alloy X-750. Materials given two different aging treated were tested. After the cracking, the fractured specimens were inspected by SEM, and the crack tip region was examined by TEM two-stage replica technique. The crack growth rate of a two-stage aged X-750 was measured using MWOL specimens.
2.2.1.1 Material and Specimens

Alloy X-750 nominally contains 73% Ni, 16% Cr, 7% Fe, 3% Ti, and 1% Nb. The material used was 1.575 mm (0.062") sheet of Alloy X-750 supplied by INCO Alloys International, Inc. The as received material was solution treated. The exact heat treatment was not known, but was estimated to be an anneal at 1000°C. The hardness of the sheet was measured by superficial hardness testing with a load of 30kg and a diamond indenter. The hardness was converted to $R_p 82$ from the Table of Standard Hardness Conversion (72). The microstructure of the solution annealed specimen is shown in Figure 14. The specimen was chemically etched in a solution consisting of 80% HCl, 13% HF and 7% HNO$_3$ (by volume). Since the material had not been aged, no carbides were observed, and the grain size was about 30μm.

Two heat treatments, one-stage and two-stage aging, were performed to study the IGSCC susceptibility of different microstructures. Before heat treatment, specimens were sealed in an evacuated quartz tube to prevent oxidation. Details of heat treatments are shown in TABLE 5.

Figure 15 and 16 show the microstructures of two-stage and one-stage aged materials, respectively. These samples were chemically etched in the same solution mentioned previously. The main difference between the two was that plenty of carbides were discontinuously
TABLE 5. Heat Treatment of Alloy X-750 Used for U-Bend Specimens

<table>
<thead>
<tr>
<th>Treatment Type</th>
<th>Temperature</th>
<th>Time</th>
<th>Coolant</th>
</tr>
</thead>
<tbody>
<tr>
<td>One-stage Aging Treatment</td>
<td>1025°C</td>
<td>1 hour</td>
<td>air cool</td>
</tr>
<tr>
<td>Aging</td>
<td>704°C</td>
<td>24 hours</td>
<td>air cool</td>
</tr>
<tr>
<td>Two-stage Aging Treatment</td>
<td>982°C</td>
<td>1 hour</td>
<td>air cool</td>
</tr>
<tr>
<td>1st aging</td>
<td>816°C</td>
<td>20 hours</td>
<td>air cool</td>
</tr>
<tr>
<td>2nd aging</td>
<td>704°C</td>
<td>24 hours</td>
<td>air cool</td>
</tr>
</tbody>
</table>

precipitated on the grain boundary of the one-stage aged specimens, while grain boundary precipitation was much less pronounced in the two-stage aged material. Both aging treatments produced the same hardness of $R_C$ 35.

The U-bend specimens were prepared following the ASTM recommended standard practice G30-79 (73). Specimen was bend around a 1.25 inch (3.175 cm) diameter steel bar. The two legs of the specimen were fixed by a 316 stainless steel bolt and nut with a separation of 3.175 cm. The dimensions of the specimen are shown in Figure 17. Specimens were then put into the autoclave for testing.

2.2.1.2 IGSCC Testing and Cracking Studies

The testing apparatus and procedures are described in Section 2A.1.2. Testing environment was in deaerated steam at 380°C with a 0.1 MPa (STP) hydrogen overpressure. The autoclave was opened up every 100 hours to check for cracking. For the more susceptible two-stage aged X-750, the checking periods were every 50 hours. If any cracks were observed during inspection, the test for that
Figure 14. Microstructure of solution annealed Alloy X-750. Chemical etch in 80% HCl, 13% HF, and 7% HNO$_3$. (a) 400x (b) 1000x.
Figure 15. Microstructure of two-stage aged Alloy X-750. Chemical etch in 80% HCl, 13% HF, and 7% HNO₃. (a) 400x (b) 1000x.
Figure 16. Microstructure of one-stage aged Alloy X-750. Chemical etch in 80% HCl, 13% HF, and 7% HNO₃. (a) 400x (b) 1000x.
Dimension in mm
L: 100.000  D: 6.528
W: 17.500  R: 15.875
T: 1.575  Y: 3.175
M: 78.472

Figure 17. U-bend specimen used in the IGSCC study of Alloy X-750 and 410SS.
specimen was terminated. The recorded fracture time of the specimen was the accumulated test time until cracks were observed. The specimen was cut for fracture studies in SEM, and replica studies of cracks in TEM.

2.2.1.3 TEM Metallographic Studies

TEM studies were carried out to characterize the microstructures, especially the grain boundary structures. To prepare the specimens, small pieces of materials were cut from the as-received sheet of X-750. Samples were heat treated in two-stage and one-stage aging. Others were left untreated as solution annealed material. To prepare thin foils for TEM studies, the first step was to reduce those specimens to around 70μm thick by mechanical grinding through silicon carbide polishing papers from 120 to 400 grit. Fine polishing was done using 0.3μm alumina powders. Then 3 mm diameter of discs were punched from the foil. Final thinning was done using a jetpolishing unit (Struers, Model TENUPOL) using a solution containing 10% (by volume) perchloric acid (70% concentrated) and 90% methyl alcohol at -50°C. A potential of 30-32V was applied, and the current was around 120mA. The thinning lasted for 30 to 60 seconds before perforation occurred. The thin region around the perforation was ready for observation.
2.2.1.4 Two-stage Replica Studies on the Fractured Specimens

TEM two-stage replica studies were done on fractured samples. Regions near the main propagating crack were mechanical polished to 400 grit silicon carbide polishing papers and then polished with 0.3μm and finally 0.05μm alumina powders. Polishing was done slantwise making an angle of about 15° with the sample surface so that the polished area revealed all cracks with different depth from the sample surface. Replicating that region followed procedures described in section 2A.1.3.

2.2.2 STUDY OF CRACK GROWTH IN MWOL SPECIMENS

MWOL specimens were used to study the IGSCC crack growth in high temperature deaerated water/steam environment. Materials in the most IGSCC susceptible (two-stage aged) condition was used for the study.

2.2.2.1 Material

The specimen came from a 1 inch diameter (2.54 cm) Alloy X-750 bar supplied by Haynes International, Inc. The chemical composition is shown in TABLE 6. The MWOL specimens were machined from that bar. The dimensions were different from that of Alloy 600. However, as long as the specimen half-height to width (H/W) was 0.486 the stress calculation in Appendix B could be used except specimen width and thickness needed to be
TABLE 6. Chemical Composition and Heat Treatment of Alloy X-750 Used for MWOL Specimens

<table>
<thead>
<tr>
<th></th>
<th>Ni+Co</th>
<th>Cr</th>
<th>Fe</th>
<th>Ti</th>
<th>Nb+Ta</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.</td>
<td>71.6</td>
<td>15.93</td>
<td>7.47</td>
<td>2.43</td>
<td>0.97</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>C</td>
<td>S</td>
<td>P</td>
<td>Mn</td>
<td>Si</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>0.04</td>
<td>&lt;0.002</td>
<td>&lt;0.005</td>
<td>0.24</td>
<td>0.19</td>
</tr>
</tbody>
</table>

B. Heat Treatment:
- solution annealing: 982°C, 1 hour, air cool
- 1st aging: 816°C, 20 hours, air cool
- 2nd aging: 704°C, 24 hours, air cool

changed. Here the specimen height was 1 inch (2.54 cm), the thickness was 0.6 inch (1.524 cm), and the width was 1.5 inch (3.81 cm). The specimen was sealed in evacuated quartz tube and heat treated by two-stage aging procedures. Figure 18a and 18b show the microstructure of the specimen. The grain boundary shows no sign of carbide precipitation. However, carbide were observed on the prior twin boundaries. Figure 18b shows grains grew from the twin boundaries during the annealing. Twin boundaries were retained because of the twin boundary carbides inhibited the grain growth across the twin boundary. The microstructure shows a duplex structure with most grains around 10-20μm and some secondary growth of grains as large as 50μm. The hardness of the specimen was R_C 32.

The specimen was fatigue pre-cracked with maximum-minimum loads of 3000-300 lbf. The frequency used was 5 Hz. After 10500 cycles the Instron was stopped and the
fatigue crack length was 2.712mm. The standard procedures of fatigue pre-cracking has been described in section 2.1.3.3.

2.2.2.2 Crack Growth Rate Measurement

Crack growth rates in two-stage aged Alloy X-750 were measured by MWOL specimens. A strain gage was attached to the back of the fatigue pre-cracked specimen and the specimen was loaded to the desired $K_I$ values. 3 different $K_I$ values were used in the experiments, specimen loaded to $K_I=60.8$ and $32.2 \text{ MPa}\sqrt{\text{m}}$, was tested at $260^\circ\text{C}$, $280^\circ\text{C}$, $300^\circ\text{C}$, $320^\circ\text{C}$, and $340^\circ\text{C}$ and the third set of measurements were done for $K_I=15.4 \text{ MPa}\sqrt{\text{m}}$ at $300^\circ\text{C}$, $320^\circ\text{C}$, $340^\circ\text{C}$, and $360^\circ\text{C}$ in 36g of deaerated water. Hydrogen overpressure (0.1MPa, STP) was added to the water at room temperature. In all measurements, the crack was exposed to the steam phase. Apparatus and procedures for data acquisition and data processing were the same as described in section 2.1.3. After the experiment, the crack growth rates were plotted against the reciprocal of temperatures, and apparent activation was obtained. The specimen was broken open and the SEM was used to examine the fracture surface.
Figure 18. Microstructure of two-stage aged X-750 for MWOL specimens. Chemical etch in 80% HCl, 13% HF, and 7% HNO₃. (a) 400x (b) 1000x.
2.3 410 STAINLESS STEEL

2.3.1 STUDY OF IGSCC OF 410SS

410 stainless steels were tempered at 4 different temperatures at 450, 500, 550, and 650°C. Hardness tests were conducted to monitor the tempering effect. The change in microstructure was characterized using the optical microscope. U-bend stress corrosion tests were done in deaerated 380°C steam. After cracking occurred the specimen was taken out and the testing time was recorded. Finally the fracture surface was examined by SEM.

2.3.1.1 Material and Specimens

410SS was supplied by Williams & Company Inc. as a 1.57 mm thick sheet. Chemical composition of the material is shown in TABLE 7:

TABLE 7 Chemical Composition and As-Received Room Temperature Mechanical Properties of 410 Stainless Steel Sheet Used in U-bend Test

<table>
<thead>
<tr>
<th>C</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Cu</th>
<th>Co</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.131</td>
<td>12.4</td>
<td>0.29</td>
<td>0.4</td>
<td>0.15</td>
<td>0.02</td>
<td>0.66</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>N₂</th>
<th>Al</th>
<th>Sn</th>
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</thead>
<tbody>
<tr>
<td>0.39</td>
<td>0.002</td>
<td>0.022</td>
<td>0.047</td>
<td>0.012</td>
<td>0.016</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>YS</th>
<th>UTS</th>
<th>Elon.%*</th>
</tr>
</thead>
<tbody>
<tr>
<td>276 MPa</td>
<td>497 MPa</td>
<td>28</td>
</tr>
</tbody>
</table>

* gage length 25 mm.
Samples were cut from the sheet and annealed at 980°C for 1 hour and water quenched. Tempering was conducted at 450°C, 500°C, 550°C and 650°C for 2 hours and air cooled. Microstructures of these differently tempered materials are shown in Figure 19, 20, 21, and 22 respectively. Specimens were electrolytically etched in oxalic acid solution (10g oxalic acid in 100 ml water) at 6V for 30 seconds. Figure 19a and 19b show the microstructure of 450°C tempered 410SS, which consisted of martensitic structure with some large carbides located inside grains, and no grain boundary precipitates was observed. Figure 20a and 20b are the microstructure of the 500°C tempered material, which show almost identical microstructure as that of the 450°C tempered 410SS. No carbides were precipitated on the grain boundary but some were found inside grains. The micrographs of 550°C tempered material are shown in Figure 21a and 21b, which show carbides precipitation in both grains and grain boundaries. Carbides formation on the former austenite grain boundaries was evident. In the microstructure of the 650°C tempered material, plenty of carbides were observed both on the grain boundary and on the martensite plates.

Hardness of 410SS for as quenched and all other samples with 2 hour tempering at 450, 500, 550, and 650°C were measured. The data obtained from superficial hardness testing were then converted to $R_C$ scale, which is shown in Figure 23. It shows that the hardness of the
martensite continuously dropped by increasing the tempering temperatures after water quench. The hardness remains above Rق26 until tempered at 650°C. The decrease of hardness by tempering at high temperatures was due to the loss of the hardening effect from overaging of $M_7C_3$ and the formation of $M_{23}C_6$ carbides. The same phenomenon is reported in other publications as given in section 1.6.1.

2.3.1.2 Testing and Metallographic Studies

Specimens tempered at 500°C, 550°C, and 650°C were used for IGSCC U-bend testing. U-bend specimens were prepared following the procedures described in section 2.2.1.1. Then specimens were put into the autoclave in 380°C steam with 0.1 MPa (STP) hydrogen overpressure. Procedures to run the stress corrosion test are described in section 2.1.1.2. Every 150 hours the furnace was shut down and specimens were taken out for inspection. Whenever cracks were observed, the specimen was terminated from testing and the fracture surface was examined in the SEM.
Figure 19. Microstructure of 410SS, tempered at 450°C for 2 hours. Electrolytic etch in oxalic acid solution. (a) 400x (b) 1000x.
Figure 20. Microstructure of 410SS, tempered at 500°C for 2 hours. Electrolytic etch in oxalic acid solution. (a) 400x (b) 1000x.
Figure 21. Microstructure of 410SS, tempered at 550°C for 2 hours. Electrolytic etch in oxalic acid solution. (a) 400x (b) 1000x.
Figure 22. Microstructure of 410SS, tempered at 650°C for 2 hours. Electrolytic etch in oxalic acid solution. (a) 400x (b) 1000x.
Figure 23. Hardness of 410SS after tempering at different temperatures.
3.1 ALLOY 600

3.1.1 IGSCC IN REVERSE U-BEND TESTING

IGSCC cracks occurred after testing for 339 hours in 380°C steam saturated with an 0.1 MPa (STP) hydrogen. Cracks were found in the inner side of the tube. Some cracks were deep enough to penetrate the whole thickness of the specimen. Thus those cracks could be opened up easily for examination in SEM. Cracks were observed in the region between the top of the rim and the bottom of the reverse bend. Shen (9) gave an analysis indicating that the site of the IGSCC was a strained and highly stressed (biaxial tension state) region. This indicates the cracking was aided by the strain and the high tensile stress.

3.1.1.1 Fractography of IGSCC in RUBs

Figure 24a shows the low magnification of the fracture surface of the cracked RUB sample. The fracture mode was completely intergranular, and the surface of the
specimen showed dark appearance, which was corrosion product that formed during the test. In a higher magnification micrograph of Figure 24b, a layer of corrosion products can be observed on the fracture surface. This region was cracked earlier and exposed to the aggressive environment during the test so the accumulated corrosion product was thick. Figure 25 shows a region with a transition from IGSCC to the final ductile tearing (dimple fracture) of the specimen. No corrosion products could be observed on the fracture surface, indicating this region is a more freshly opened fracture surface. Some intergranular secondary cracking occurred on the surface.

According to the void-linkage model, one might expect to find plenty of depressions on the facets of grains on the fracture surface. However, in Figure 25 the grain facets appeared to be flat and smooth. Those facets emerged after the final stage of cracking where voids had already linked up and become crack-like. Thus no voids can be observed in this stage. To verify the model, one has to examine the precursor of the cracking where voids were in the early growth stage. This means that microvoids could be found in the crack tip region in which microvoids were continuously nucleated during the crack advancement.

The crack tip could be seen by opening up the IGSCC crack at room temperature and examining the region at the
Figure 24. Fracture surface of a RUB sample tested in steam saturated with 0.1 MPa H₂ (STP) at 380°C. (a) low magnification (b) high magnification.
Figure 25. Fracture surface near transition of IGSCC to ductile tearing in a RUB sample tested in steam saturated with 0.1 MPa (STP) H$_2$ at 380°C.
transition of the intergranular cracking to the ductile dimpled fracture. However, because the voids were very fine and discrete, the tearing in the fracture process would destroy those voids. The best way to resolve the microvoids were to section the cracks, use two-stage replica technique to replicate the tip of the crack, and examine the tip region using TEM.

3.1.1.2 Replica Studies of IGSCC in RUB Specimen

With the aid of Figure 6, the relationship between the topography of the specimen and the feature in the replica are explained as following. In the shadowing and carbon depositing processes, the replicating tape was placed with the imprinted image of the face up. The topography of the tape was just opposite to that of the fracture surface. This means a void on the fracture surface became a dome, and a crack in the sample showed up as a ridge on the tape. During the shadowing process, the region facing the platinum particle source received the highest intensity of deposition and left a platinum free shadow behind the peak. A horizontal region had an angle of 20° to the platinum beam, thus received moderate deposition of platinum. Since platinum scattered electrons in the TEM, regions with more platinum deposition would appear darker than the less deposited region. Hence a hump in the replica (depression in the
sample) would appear as a black rim along with a shadow of white tail in back of the rim, and the flat region of the sample would be grey.

Figure 26 shows the shadowed replica of a region including an IGSCC main crack (indicated by the arrow marked A) and some fine grain boundary cracking ahead of it. It shows that fine discrete bubbles (black dots with white tails) nucleated ahead of the main crack. They grew and finally linked up into crack. The contrast at the crack (a ridge in the replica) indicated that these bubbles had already joined together to become crack-like. This explains why the fracture surface of grain facets appeared smooth and flat.

Examining regions farther from the main crack, no such grain boundary bubbles were observed. Thus only those boundaries very close to the main crack were attacked. In the present case, the farthest bubbles (indicated by arrows marked B in Figure 26) were 17 μm away from the tip of the crack. Since those bubbles were discrete in nature, they did not have direct contact with the corrosion environment. This the evidence that the IGSCC of Alloy 600 in high temperature deaerated water is not caused by direct anodic dissolution. However, the hydrogen induced void-linkage model (section 1.5) suggests that corrosion generated hydrogen diffuses into the metal and reacts with carbon to form methane bubbles on the grain boundary. The hydrogen was produced by corrosion at
Figure 26. Two-stage replica micrograph of a region ahead of an IGSCC crack.
the tip of the crack. Thus grain boundary bubbles could only be observed at a region very close to the hydrogen source where the hydrogen concentration was highest.

The kinetic of the IGSCC cracking includes the nucleation and growth of grain boundary bubbles. The crack propagates through the linkage of bubbles and finally leads to the fracture. To understand the initiation of the bubbles, one could examine the region farthest from the main crack where the bubbles were just formed. Figure 27a is another replica micrograph from the same sample as Figure 26. The main crack is on the upper right corner of the picture. Ahead of it the precursor of grain boundary cracking is shown, which is indicated by small discrete bubbles. Figure 27b shows higher magnification of the region indicated by arrow mark in Figure 27a. Here grain boundary bubbles were well defined and discrete, thus this was in the early stage of bubble nucleation. Examining closely, the distribution and size of bubbles were different. Bubbles indicated by arrows marked 'A' were evenly apart at a distance of 0.2\(\mu\)m, and their size was around 0.05\(\mu\)m. The even bubble spacing and same bubble size of these bubbles dictated that these bubbles were formed at the same time and possibly from the same mechanism. In between these larger 'A' bubbles, there were two or three smaller ones indicated by arrow mark and 'B' with a size around 0.01-0.02\(\mu\)m. This suggested these smaller 'B' bubbles nucleated after those 'A' bubbles.
Figure 27. two-stage replica micrograph of a region containing IGSCC cracks and precursor grain boundary bubbles
(a) bubble nucleation ahead of an IGSCC crack
(b) high magnification in the region indicated by arrow mark in (a).
3.1.1.3 Effect of Slip Line Impingement at Grain Boundaries

Figure 28 shows the replica of the surface that was bent to introduce plastic deformation, in which parts of two grains are shown. Apparently, after the bending, primary slip systems were activated in both grains. Those lines are parallel to each other indicating that they are in the same slip system during the bending. Since the specimen was electro-polished in advance, the specimen surface was extremely smooth before the bending and all shadows of slip lines came after the mechanical bending. Shadows of the straight lines were generated from surface offset caused by the accumulation of displacement from dislocation motions. Each slip line contains large number of dislocations piling up on the grain boundary, which exerted a high stress concentration on the grain boundary. The stress concentration might be high enough to nucleate microvoids at the site of impingement. To verify this hypothesis the slip line spacing was measured and compared to the bubble spacing ahead of the IGSCC crack.

The average slip line spacing in Figure 28 was around 0.2±m. This spacing was exactly the same as the average spacing between those larger 'A' bubbles. Thus it is quite possible that the larger bubbles were formed from slip-line impingement induced microvoids on the grain boundary. However, the mechanism of the formation of those small 'B' bubbles is still unclear. One needs to
Figure 28. Two-stage replica micrograph of the slip lines on the surface in a bent Alloy 600 specimen.
know what causes the nucleation of new bubbles, and why they locate right at the center between those large bubbles? The stress field induced by high methane pressure in the grain boundary bubble could be the driving force for the nucleation of new bubbles. Patharentathy (74) and Shewmon (75) have shown that the tensile stress normal to the grain boundary between two methane bubbles would be extremely high. Thus it is believed that this high stress induced by methane pressure plus the external applied stress normal to the boundary was the driving force to nucleate these new bubbles. Also, the distribution of the stress fields explained why the small bubbles formed at the center between large bubbles. Details of the analysis is given in Section 4.1.2.

3.1.2 CRACK GROWTH RATE STUDIES IN MWOL SPECIMENS

3.1.2.1 Fractography of IGSCC in MWOL Specimen

IGSCC fracture of the MWOL specimen was bounded by the pretest and post-test fatigue fracture surface. Figure 29a shows MWOL specimens before testing. After the experiments the specimen was opened up for examination. In Figure 29b, A is the start of the pretest fatigue fracture surface. B is the end of the fatigue fracture and the start of the IGSCC fracture. This entire region shows dark appearance from the corrosion product formed during the test. The shining fracture region C is the post-test
fracture, and the final region is the saw cut. Thus the crack length could be known by measuring the IGSCC cracking between those two well defined fatigue fracture.

Figure 30a is the low magnification SEM fractography of the IGSCC fracture. Region A is the fatigue precrack, and B is the IGSCC fracture. The arrow shows the direction of the IGSCC crack propagation. Several fingers of IGSCC cracks grew faster than the main crack front. The average crack length is around 2 mm, which agrees with the length of 2.14 mm calculated from Klintworth's calibration curve (Appendix C). Figure 30b shows the tip of one of the IGSCC fingers embedded in the post-test fatigue fracture. It clearly shows the fracture was grain boundary fracture. Since the crack opening displacement was constant for this specimen, $K_I$ value decreased as the crack grew longer. The crack growth rate was measured as $K_I$ decreased from an initial 60 MPa/m to a final 55 MPa/m. The calculation of $K_I$ was made using the changes in crack length calculated from the potential drop data.
Figure 29. MWOL specimen used in the crack growth measurement (a) before testing (b) after testing. A is the start of the fatigue precrack, B is the start of the IGSCC.
Figure 30. SEM micrograph of fracture surface of the MWOL specimen tested in high temperature steam.
(a) low magnification
(b) crack tip ahead of the main crack front.
3.1.2.2 Crack Growth Rate and Apparent Activation Energy

Under isothermal testing, the crack length measured linearly with time. Figure 31 through 34 are the plots for testing at 320, 340, 360, and 380°C, respectively. The plots indicate constant crack growth rates in each test. The slope from the linear best fit equation for the data gives the crack growth rate for that test temperature. TABLE 8 shows the crack growth rates for the experiments initially at \( K_I = 60 \text{ MPa}/\text{m} \), for these temperatures. Also, data obtained by Shen (42) for initial \( K = 80 \text{ MPa}/\text{m} \) are included. Plotting \( \ln(da/dt) \) vs. \( 1/T \) for those two sets of testing, two activation energies were obtained for each initial \( K_I \). The temperature dependence of the crack growth rates for each \( K_I \) are shown in Figure 35 and Figure 36. The activation energy was 80 kJ/mol for \( K_I \) in the range of 80 to 72 MPa/m, and was 168 kJ/mol for \( K_I \) in the range of 60 to 55 MPa/m.
TABLE 8. Crack Growth Rates vs. Temperature for Two Sets of $K_I$ Values

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>da/dt (m/sec) [2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>$1.31 \times 10^{-11}$</td>
</tr>
<tr>
<td>340</td>
<td>$3.46 \times 10^{-11}$</td>
</tr>
<tr>
<td>360</td>
<td>$1.08 \times 10^{-10}$</td>
</tr>
<tr>
<td>380</td>
<td>$2.94 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

(II). $K_I=80$ MPa/m, [1],[3]

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>da/dt (m/sec) [2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>$8.83 \times 10^{-11}$</td>
</tr>
<tr>
<td>340</td>
<td>$2.53 \times 10^{-10}$</td>
</tr>
<tr>
<td>360</td>
<td>$4.03 \times 10^{-10}$</td>
</tr>
<tr>
<td>380</td>
<td>$4.72 \times 10^{-10}$</td>
</tr>
<tr>
<td>420</td>
<td>$1.11 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

[1]- Initial loaded $K_I$ values.
[2]- Based on the best linear fit of the crack length/time data of MWOL specimens.
[3]- Data from reference 42.

Using an equation of the form $\frac{da}{dt} = AK_I^n$ for each temperature and initial $K_I$ values for the crack growth, the exponents of $K_I$ were obtained. The exponent $n$ for 320, 340, 360, and 380°C are shown in TABLE 9.

TABLE 9. The $K_I$ Dependence of the Crack Growth Rates in Alloy 600 at Different Temperatures

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$n^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>6.6</td>
</tr>
<tr>
<td>340</td>
<td>6.9</td>
</tr>
<tr>
<td>360</td>
<td>4.5</td>
</tr>
<tr>
<td>380</td>
<td>1.7</td>
</tr>
</tbody>
</table>

* - Using the Relation of $\frac{da}{dt} = AK_I^n$

Thus at lower temperatures crack growth rate varies as a high power of the stress intensity with an $n$ of almost 7. At 380°C the exponent $n$ was 1.7.
Figure 31. Crack length vs. time curve at 320°C, initial $K_I=60$ MPa/m.
Figure 32. Crack length vs. time curve at 340°C, initial $K_I=60$ MPa/m.
Figure 33. Crack length vs. time curve at 360°C, initial $K_I=60$ MPa/m.
Figure 34. Crack length vs. time curve at 380°C, initial $K_I=60$ MPa/m.
Figure 35. Temperature dependence of the crack growth rates, $K_I = 60$ MPa/m.
Figure 36. Temperature dependence of the crack growth rates, $K_I=80$ MPa/m. (9)
3.2 ALLOY X-750

3.2.1 ELECTRON MICROSCOPY RESULTS

3.2.1.1 Solution Treated (As-Received) Alloy X-750

The as-received Alloy X-750 specimen was solution annealed at approximate 1000°C. Figure 37a and 37b show the typical TEM bright-field images of the microstructure of the material. The results confirm the optical observation in Figure 14a and 14b that carbides have not formed in the microstructure. Furthermore, no $\gamma'$ particles are observed, since an age hardening anneal was not performed. Figure 37a shows a triple junction of three grains. No precipitates of any kind could be found in the matrix or on the grain boundaries. Thus, the solution annealed microstructure would be very soft, as indicated by a hardness near $R_B$ 82. Figure 37b gives a high magnification view on the grain boundary. A typical dislocation pileup is shown in the micrograph. These were occasionally observed in the microstructure. Examining the grain boundaries again shows was straight and free of carbides.

3.2.1.2 Two-stage aged Alloy X-750

After solution anneal at 982°C for one hour, the specimen was aged for two steps at 816°C for 20 hours and 704°C for 24 hours. Figures 38a and b are TEM bright-
Figure 37. Microstructures (TEM multi-beam bright field images) in the solution annealed Alloy X-750 sample.
(a) a region contains triple junction of three grains
(b) a segment of grain boundary.
field images of the material. Figure 38a shows parts of two grains separated by a grain boundary. Numerous γ' particles (fine dark spots) were formed during the aging. Their distribution was uniform throughout the matrix and their size was uniform as well. This indicates that γ' particles were formed by a homogeneous nucleation process (continuous precipitation). In the upper grain in the micrograph, there are two large particles (indicated by arrow marks) inside the grain. Energy dispersive spectroscopy (EDS) analysis indicated these are titanium and niobium rich MC carbides. They are undissolved primary carbides due to the low solution anneal temperature.

Examination of the material at high magnification gives the microstructure shown in Figure 38b. This shows a short segment of grain boundary and a corner of the second grain locate at the right part of the picture. The image of γ' phase comes from the coherent strain fields around each γ' precipitate. The average size of these γ' particles is estimated to be 0.06μm. However, this could be an overestimate because the strain field is slightly larger than the real size of the particle. It is important to note that no carbides formed on the grain boundary. On the other hand, γ' particles are observed throughout the microstructure including the grain boundary region.
Figure 38. Microstructures (TEM bright-field images) in two-stage aged Alloy X-750 sample.
(a) a region includes 2 grains
(b) high magnification of the grain boundary and the γ' particles.
3.2.1.3 One-stage aged material

One-stage aged material was solution annealed at 1025°C for one hour and aged at 704°C for 24 hours. Since the solution temperature is higher, thus more carbides than that in the two-stage aged alloy were re-dissolved, supplying carbon for the formation of grain boundary carbides during the later aging treatment. Constituents on the grain boundary of one-stage aged material was very different from the two-stage aged. The TEM bright-field micrographs are shown in Figures 39a, b and c.

In Figure 39a, a junction of three grains are shown. Carbide precipitation was observed on almost all grain boundaries. EDS identified those carbides as chromium rich carbides. The morphology of the carbides indicated that the carbides were formed by discontinuous precipitation. These carbides were plate-like and sometimes is called cellular precipitation. In addition, grain boundary migration was induced through the growth of carbide plates. The carbides first nucleated at the grain boundary but later grew alternately into grains on the opposite side of the boundary. Thus the inter-plate matrix phases were alternately coherent to the two grains.

Another type of grain boundary precipitates are shown by the arrows marked 'A' in Figure 39b. They distribute discretely on the grain boundary with irregular or angular shape, and may appear with the cellular chromium carbides. EDS results show that they are titanium and niobium rich
precipitates. They are presumably partially decomposed grain boundary MC carbides. If those MC carbides dissolved during the solution treatment, the released carbon could supply subsequent grain boundary chromium carbide precipitation. Cellular chromium carbides indicated by arrows marked 'B' are shown in the same figure, which could form by this process.

Figure 39c shows the high magnification of the microstructure. It shows the grain boundary chromium carbides and the intragranular γ' precipitates. The uniform distribution of the γ' particles indicates continuous precipitation process. The size of the γ' particles is around 0.01μm, which is much smaller than γ' particles in the two-stage aged materials. Thus the size of the γ' particles increases with the temperature and time of the aging process.

3.2.2 IGSCC OF ALLOY X-750 IN U-BEND SPECIMENS

3.2.2.1 Test Results

Figure 40 shows the U-bend specimens before and after the testing. TABLE 10 shows the failure time of U-bend tests in solution annealed, two-stage aged, and one-stage aged materials.
Figure 39. Microstructure (TEM bright-field images) in one-stage aged Alloy X-750 sample.
(a) A triple junction of 3 grains, chromium carbides were formed on grain boundaries.
(b) Discrete precipitates on the grain boundary.
Figure 39. (continued)
(c) high magnification micrograph of the grain boundary chromium carbides.
TABLE 10 Results of U-bend Tests in Different
Microstructures

<table>
<thead>
<tr>
<th>Materials</th>
<th>Temp. (°C)</th>
<th>$P_{H_2}$ (MPa)</th>
<th>Time to fracture (Hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soln. Annl.</td>
<td>380</td>
<td>0.1</td>
<td>&gt;2059, no cracks</td>
</tr>
<tr>
<td>One-stage aged</td>
<td>380</td>
<td>0.1</td>
<td>1681</td>
</tr>
<tr>
<td>Two-stage aged</td>
<td>380</td>
<td>0.1</td>
<td>139, 146</td>
</tr>
</tbody>
</table>

The testing conditions for the three different materials were kept identical. Hence the difference in fracture time stemmed purely from the difference in microstructure. Testing the solution annealed material lasted the longest time and the specimen was still not cracked when the test was terminated after 2059 hours. Cracking of the two-stage aged materials was the easiest among the three, cracks were observed after around 140 hours in two test specimens. Cracks occurred near the center and outside rim of the U-bend (where the tensile stress is highest) running perpendicular to the length of the specimens. The main crack propagated through the specimens so the specimens were broken half. Along with the through-thickness crack, there were a family of smaller cracks parallel to it. The large crack grew faster than the others, thus it relieved the load and stopped the growth of the smaller cracks. All cracks are normal to the applied tensile stress.

Cracks were observed in one-stage aged U-bend specimen after testing for 1681 hours, an order of magnitude longer than required for two-stage aged
Figure 40. U-bend specimens before and after the testing.
specimens. The cracks also occurred at the same location and the fracture mode was the same as the two-stage aged Alloy X-750.

The crack growth rates could be roughly estimated from TABLE 10 by dividing the thickness of the specimens (1.5748 mm) by the fracture time. The results show that for two-stage aged materials, the rate was approximately $3.1 \times 10^{-9}$ m/s, whereas the rate for one-stage aged was $2.6 \times 10^{-10}$ m/s. These crack growth rates were an underestimate because the fracture time also included the crack initiation time. Nonetheless, the crack growth rates for the two-stage aged materials were one order of magnitude faster than the one-stage aged. The tendency that crack growth in two-stage aged materials was faster than the one-stage aged was consistent with the works reported by Wilson and Mager (36).

3.2.3 SEM OBSERVATION OF IGSCC IN U-BEND SPECIMENS

3.2.3.1 Two-Stage Aged Specimens

Figures 41a and b show the fracture surface of a two-stage aged U-bend specimen fractured in 139 hours in 380°C steam saturated with 0.1 MPa (STP) hydrogen. Cracks started from the upper rim of the specimen (indicated by arrow mark in 41a), where the applied load from the bolt exerted a tension on the surface. The crack propagation is normal to the tensile direction, thus the failure was
produced by mode I fracture. The complete grain boundary cracking in Figure 41a indicates the failure was IGSCC. Figure 41b shows a high magnification of the fractured grain facets in the same specimen. Some roughness which could be grain boundary precipitates can be observed on the facets. Mechanically, decohesion might occur between the interface of precipitates and the grains. However, since the precipitates do not cover all the fracture surface, they seemed not to be the major reason for the complete grain boundary separation. In the same picture, some secondary cracks exist along with the main fracture path. These ran into the fracture plane.

Figure 42a is a SEM micrograph of a sample which was slightly polished with 400 grit silicon carbide paper to remove the surface scratch and corrosion product. The final polished was carried out using 0.05μm alumina powder. Surface cracks can be observed on all the grain boundaries. These surface cracks are believed to form at the earlier stage of the IGSCC. The arrows show the axis of the tensile stress on the specimen. The cracks running normal to the tensile axis were wider than the other, which indicated that the crack growth was enhanced by tension. Given enough high tensile stress, these surface cracks would grow deeper into the sample. Figure 42b shows one of the fine surface cracks, which was formed by the formation and link up of small grain boundary voids. Inside the crack (indicated by arrow marks), microvoids
Figure 41. Fracture surface of a two-stage aged Alloy X-750 U-bend specimen tested in steam saturated with 0.1 MPa H₂ at 380°C.  
(a) low magnification  
(b) high magnification.
Figure 42. Slightly polished surface of two-stage aged Alloy X-750 U-bend specimen tested in 380°C steam saturated with 0.1 MPa hydrogen (STP) for 139 hours.
(a) low magnification micrograph
(b) high magnification of one of the fine cracks in (a).
can be identified and some of them have already linked up and become a continuous crack. After polishing into the surface to a depth of a few hundreds micrometers, these surface cracks were no longer observed. Since the crack growth was stress assisted, the growth of the main crack (which eventually broke the specimen) relieved the tension load and the growth of other fine cracks was stopped.

Figure 43a shows an area near the main crack at 600x which was located at the right corner of the graph. A fine crack indicated by an arrow mark is shown in Figure 43b, at a magnification of 15000x. The picture clearly shows the IGSCC fracture came from void nucleation and linkage mechanism. The elongated shape of the voids indicated that each void is the linkage of two or three voids, and ligaments still exist between those voids.

3.2.3.2 One-Stage Aged Specimens

Examining the one-stage aged sample, the feature of the fracture surface suggests that the fracture mode is also IGSCC throughout the fracture surface. Figure 44a shows the fracture of the U-bend sample tested in 380°C hydrogenated steam. The specimen fractured completely by grain boundary cracking. The IGSCC at a higher magnification is shown in Figure 44b. Some secondary cracks also exist as in the two-stage aged materials. In addition, SEM micrograph of the unpolished surface shows the grain boundary cracks on the surface. Comparison with
Figure 43. Polished and unetched sample containing the IGSCC cracking in a two-stage aged U-bend specimen.
(a) low magnification micrograph containing a main propagating crack
Figure 43. (continued).
(b) high magnification of the crack indicated by an arrow in (a).
Figure 44. Fracture surface of a one-stage aged U-bend specimen fractured after tested for 1681 hours in 380°C hydrogenated steam.
(a) low magnification
(b) high magnification.
the two-stage aged materials, the one-stage aged material contains less surface cracks and less minor cracks parallel to the main fracturing crack. This agrees with the tests results that showed the one-stage aged material is less IGSCC susceptible than the two-stage aged specimens in the high temperature deaerated water.

3.2.4. TEM REPLICA RESULTS OF THE IGSCC IN TWO-STAGE AGED ALLOY X-750

Figure 45 is a TEM replica from a surface crack in the U-bend specimen of a two-stage aged material, which was one of the small cracks next to the main crack in Figure 43a. Those cracks is in the early stage of IGSCC in Alloy X-750. The micrograph shows discrete microvoids formed ahead of the crack. These voids nucleated as tiny bubbles on the grain boundaries. Bubbles were observed at the lower side of the graph. The bubble spacing was around 0.1-0.2μm and the bubble size was 0.03μm, and both numbers agree with the observation of boundary bubbles in Alloy 600.
Figure 45. TEM replica of a surface crack in two-stage aged U-bend specimen.
3.2.5 MWOL SPECIMEN RESULTS

3.2.5.1 Fractography of IGSCC in MWOL Specimen

IGSCC fracture of two-stage aged Alloy X-750 in MWOL specimen started after the pretest fatigue fracture surface. Figure 46 shows the fracture surface of the MWOL specimen. Arrow mark indicates the start of the IGSCC fracture. Both the pretest fatigue and IGSCC surface are dark appearance, which comes from the corrosion product formed during the test. The final shining fracture is the post-test fracture. Figure 47 shows the SEM fractography at the start of the IGSCC fracture, and the arrow shows the direction of the crack propagation. This shows the crack growth started from the IGSCC fracture into the specimen. Region 'F' in Figure 47 is the fatigue precrack.
Figure 46. Fracture surface of the MWOL specimen of the two-stage aged Alloy X-750.
Figure 47. SEM micrograph of the fracture surface in Figure 46.
3.2.5.2 Crack Growth Rate and Apparent Activation Energy

Crack growth rates were measured for initial applied stress intensities of 60.8 and 32.2 MPa/m at 260, 280, 300, 320, and 340°C. For $K_I=15.4$ MPa/m, the tests were conducted at 300, 320, 340, and 360°C. Since the MWOL specimen is a constant displacement specimen, the $K_I$ value decreases as the crack grows. The final $K_I$ decreased to 56.5, 31.0, and 15.0 MPa/m for initial $K_I$ equal to 60.8, 32.2, and 15.4 MPa/m, respectively. Figure 48-52 show the plot of crack length vs. the testing time for initial $K_I = 60.8$ MPa/m. The plots gave a straight line, indicating constant crack growth rates during the isothermal holding in the test. Crack growth rates could be obtained from slopes of the linear best fit equations from the plots. Figure 48 through 52 are the results for initial $K_I=60.8$ MPa/m. Figure 53 through 57 show the results for initial $K_I = 32.2$ MPa/m, and Figure 58 through 61 give the results for initial $K_I = 15.4$ MPa/m. TABLE 11 shows the crack growth rates of the experiments from three sets of $K_I$ values in different temperatures.
TABLE 11. Crack Growth Rates at Different Temperatures Measured from MWOL Specimen of Two-Stage Aged Alloy X-750.

(I). $K_I=60.8$ MPa/m, [1]

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$da/dt$ (m/sec) [2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>4.73 x 10^{-10}</td>
</tr>
<tr>
<td>280</td>
<td>9.18 x 10^{-10}</td>
</tr>
<tr>
<td>300</td>
<td>1.64 x 10^{-9}</td>
</tr>
<tr>
<td>320</td>
<td>3.00 x 10^{-9}</td>
</tr>
<tr>
<td>340</td>
<td>6.14 x 10^{-9}</td>
</tr>
</tbody>
</table>

(II). $K_I=32.2$ MPa/m, [1]

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$da/dt$ (m/sec) [2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>1.62 x 10^{-10}</td>
</tr>
<tr>
<td>280</td>
<td>3.29 x 10^{-10}</td>
</tr>
<tr>
<td>300</td>
<td>9.24 x 10^{-10}</td>
</tr>
<tr>
<td>320</td>
<td>2.29 x 10^{-9}</td>
</tr>
<tr>
<td>340</td>
<td>4.39 x 10^{-9}</td>
</tr>
</tbody>
</table>

(I). $K_I=15.4$ MPa/m, [1]

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$da/dt$ (m/sec) [2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>3.13 x 10^{-11}</td>
</tr>
<tr>
<td>320</td>
<td>1.90 x 10^{-10}</td>
</tr>
<tr>
<td>340</td>
<td>6.11 x 10^{-10}</td>
</tr>
<tr>
<td>360</td>
<td>2.30 x 10^{-9}</td>
</tr>
</tbody>
</table>

[1] Initial loaded $K_I$ values.
[2] Based on the best linear fit of the crack length/time data of MWOL specimens.

Plotting ln($da/dt$) vs. 1/T for those tests, activation energies for each $K_I$ were obtained. The temperature dependence of the crack growth rates for each $K_I$ are shown in Figure 62, 63, and 64. The activation energy was 86 kJ/mol for initial $K_I=60.8$ MPa/m, 116 kJ/mol for $K_I=32.2$ MPa/m, and 212 MPa/m for $K_I=15.4$ MPa/m. This observation is the same as that in Alloy 600, indicating that a higher applied stress intensity gives faster crack growth rate and a lower activation energy and a lower stress intensity gives lower crack growth rates and a higher activation energy.
Figure 48. Crack length vs. time curve at 260°C, initial \( K_I = 60.8 \text{ MPa/m} \).
Figure 49. Crack length vs. time curve at 280°C, initial $K_I=60.8$ MPa/m.
Figure 50. Crack length vs. time curve at 300°C, initial $K_I = 60.8$ MPa/m.
Figure 51. Crack length vs. time curve at 320°C, initial $K_I=60.8$ MPa/m.
Figure 52. Crack length vs. time curve at 340°C, initial $K_I=60.8 \text{ MPa} \cdot \text{m}$. 
Figure 53. Crack length vs. time curve at 260°C, initial $K_I=32.2$ MPa$\sqrt{m}$. 
Figure 54. Crack length vs. time curve at 280°C, initial $K_I = 32.2$ MPa/m.
Figure 55. Crack length vs. time curve at 300°C, initial $K_I=32.2$ MPa/m.
Figure 56. Crack length vs. time curve at 320°C, initial $K_I=32.2$ MPa/m.
Figure 57. Crack length vs. time curve at 340°C, initial $K_I = 32.2$ MPa$\cdot$m.
Figure 58. Crack length vs. time curve at 300°C, initial $K_I=15.4$ MPa/m.
Figure 59. Crack length vs. time curve at 320°C, initial $K_I = 15.4$ MPa√m.
Figure 60. Crack length vs. time curve at 340°C, initial $K_I=15.4$ MPa/m.
Figure 61. Crack length vs. time curve at 360°C, initial $K_I = 15.4$ MPa/m.
Figure 62. Ln (da/dt) vs. reciprocal of temperature curve for initial $K_T = 60.8 \text{ MPa/m}$ in different temperatures.
Figure 63. Ln (da/dt) vs. reciprocal of temperature curve for initial $K_I = 32.2$ MPa/m in different temperatures.
Figure 64. $\ln (\frac{da}{dt})$ vs. reciprocal of temperature curve for initial $K_T = 15.4$ MPa/m in different temperatures.
3.3 410 STAINLESS STEEL

3.3.1 IGSCC OF 410SS IN U-BEND SPECIMENS

3.3.1.1 Time to Fracture

Tempering at 650°C gave the most IGSCC resistant material in high temperature water. Whereas a 550°C tempering makes the material very susceptible to IGSCC failure. Thus the tendency to IGSCC cracking was the same as the room temperature embrittlement in 410SS, in which a low toughness trough appears after 500-550°C tempering. TABLE 12 summarizes the failure time of U-bend tests in 410SS with different tempering temperatures. The hardness of each material was also shown in the TABLE 12.

**TABLE 12 Results of U-bend Tests in Different Microstructures**

<table>
<thead>
<tr>
<th>Tempering Temp.</th>
<th>R_C</th>
<th>Temp.</th>
<th>P_{H2}(STP)</th>
<th>Time to fracture</th>
</tr>
</thead>
<tbody>
<tr>
<td>(°C)</td>
<td></td>
<td>(°C)</td>
<td>(MPa)</td>
<td>(Hours)</td>
</tr>
<tr>
<td>500</td>
<td>41</td>
<td>380</td>
<td>0.1</td>
<td>1131</td>
</tr>
<tr>
<td>550</td>
<td>43</td>
<td>380</td>
<td>0.1</td>
<td>508</td>
</tr>
<tr>
<td>650</td>
<td>26</td>
<td>380</td>
<td>0.1</td>
<td>&gt;2547, no cracking</td>
</tr>
</tbody>
</table>

3.3.1.2 Fracture Surface of IGSCC in 410SS

3.3.1.2.1 550°C Tempered U-bend Specimen

IGSCC occurred in 508 hours in a 410SS U-bend specimen tempered for 2 hours at 550°C. Fracture started at the high tension side of the bend. Figure 65 shows the U-bend specimens before and after the testing. It shows the fracture occurred at the highly stressed portion in
Figure 65. 410SS U-bend specimen, before and after the test.
the specimen. Figure 66 shows the fracture surface of the specimen. The fracture mode was mainly along prior austenite grain boundaries. The region near the edge of the specimen (indicated by arrows) has the thickest corrosion products (bound by two arrow marks), suggesting which had exposed longest to the environment. It indicates this was the crack initiation site. The IGSCC region extended 0.6 mm into the 1.57 mm thick specimen. Then the crack changed to transgranular fracture which was caused by overloading from high tensile stress on the uncracked area. Figure 67a shows the transition of the IGSCC to the transgranular cracking. It seems that the grain boundary cracking just stopped there and cut into grains in a transgranular mode. Figure 67b shows the final fracture on the other side of the specimen opposite to the crack initiation region. This region is totally transgranular.

Figure 67c is the fracture surface inside the IGSCC region shown in Figure 66. The fracture completely follows the grain boundary and some cracks grow perpendicularly to main crack propagation plane. Figure 67d is a high magnification micrograph for one of the grains in Figure 67c (indicated by an arrow mark), showing the grain facet in the intergranular cracking. Inspecting the edge of the specimen on the tension side, several other regions showed grain boundary cracking, with corrosion product formed on the grain facets. Thus
Figure 66. Fracture surface of 550°C tempered 410SS U-bend specimen tested in 380°C hydrogenated steam.
Figure 67. Fracture surface of 550°C tempered 410SS U-bend specimen tested in 380°C hydrogenated steam.
(a) transition of IGSCC to the transgranular cracking.
(b) final fracture.
Figure 67. continued.
(c) IGSCC fracture
(d) high magnification for one of the grains in 67c.
intergranular cracking also started in those sites although the extent of the IGSCC cracking was smaller.

To summarize, the cracking path of this U-bend specimen could be traced out from the observation on the fracture surface. Initially, the intergranular cracks started on the tension side of the specimen, propagating along the grain boundary. Then those cracks grew to an extent that the uncracked region was too small to resist the bending load. And the crack propagated rapidly through the whole specimen in a transgranular mode.

3.3.1.2.2 500°C Tempered U-bend Specimen

The U-bend specimen fractured after 1131 hours of testing. The fracture showed several IGSCC regions initiated in the tension side of the bend. The fracture surface appears exactly the same as the 550°C tempered material. Figure 68a shows one of the IGSCC region. The crack initiation site is at the upper portion of the graph, where thick corrosion product can be found. The crack propagated downward into the specimen, from which the corrosion becomes thinker. Final transgranular fracture occurred after the loading exceeded the fracture strength of the material. Figure 68b shows a high magnification of 68a for the transition from IGSCC into the transgranular fracture. Some corrosion product (indicated by C mark) can be found on the grain facets of
Figure 68. Fracture surface of 500°C tempered 410SS U-bend specimen tested in 380°C hydrogenated steam.
(a) initiation of IGSCC fracture
(b) transition of IGSCC to transgranular cleavage.
Figure 68. continued.
(c) intergranular cracking inside the transgranular fracture.
the grain boundary fracture, suggesting those grains have cracked for a period of time, exposing the fracture surface to the corrosive environment. The final fast fracture is shown in Figure 68c, which follows transgranular path, but some percentage of the fracture still follows grain boundaries. This suggests the grain boundary in 500°C tempered 410SS is intrinsically weak and grain boundary decohesion might occur for a crack propagating in the material. Results in the next section give more evidence to this conclusion.

3.3.2 TEMPER EMBRITTLEMENT OF 410SS

Specimens were broken at room temperature by bending after tempering at 450 and 500°C for 2 hours. The embrittling temperature range in the present study was consistent with reports in the literature (1.6.3). The fracture started at the tension side of the bend as in the previous IGSCC case. Figure 69a and 69b show the brittle fracture surface of the specimens tempered at 450 and 500°C, respectively. The fracture included both intergranular and transgranular cracking. The transgranular fracture was the same as that observed in the final fracture of the U-bend test shown in Figure 67b.

Figure 70 shows the intergranular fracture surface of the 450°C temper embrittled specimen. The fracture path was purely along the grain boundary, with flat and smooth grain facets on the fracture surface. The bending tests
were done in ambient environment, where no outside aggressive environment was present. Thus the brittle fracture indicates that the grain boundary was intrinsically embrittled. Since the 450°C tempered material had no carbides formed on the grain boundary (Figure 19), the embrittlement couldn't be caused by the grain boundary carbides. A plausible hypothesis is that detrimental species segregated to the grain boundary and decreased the cohesive strength of the grain boundary.
Figure 69 Fracture surface of specimens failed at room temperature.
(a) 450°C tempered specimen
(b) 500°C tempered specimen.
Figure 70. Fracture surface of a 450°C tempered specimen failed at room temperature.
CHAPTER IV

DISCUSSION

4.1 NUCLEATION OF METHANE BUBBLES ON THE GRAIN BOUNDARY IN ALLOY 600

The following discussion of the nucleation of methane bubbles on grain boundaries will address two questions:
1. How is the nucleation of the first set of bubbles assisted by slip impingement on the grain boundary and high methane pressure inside the void nuclei?
2. What is the mechanism for the nucleation of a second set of bubbles between the first set of bubbles? Why does nucleation occur at the center between two previous formed bubbles?

The nucleation of grain boundary methane bubbles includes two steps. The nucleation of the first set of bubbles is assisted by slip impingement at the grain boundary. After building up high methane pressure in the first set of bubbles, new bubbles may nucleate between existing bubbles due to the high tensile stress field between them. Figure 71 shows the sequences of the nucleation of grain boundary bubbles in the IGSCC of Alloy 600 in high temperature water. The nucleation of bubbles is discussed in the next two sections.

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Figure 71. A schematic diagram of the model of the nucleation of methane bubbles on the grain boundary. (a) nucleation of A bubbles by the slip impingement on the g.b. (b) nucleation of B bubbles between existing bubbles (c) continuation of the bubble nucleation processes (d) bubbles link up to form IGSCC fracture.
4.1.1 NUCLEATION OF THE FIRST SET OF GRAIN BOUNDARY METHANE BUBBLES

Slip impingement produces offsets on the grain boundary which can serve as the site of microvoid nucleation. Gifkins (76) proposed that slip impingement on the grain boundary generates accommodation slip in the other grain and produces a jog on the grain boundary. Then the tensile stress from dislocation pile-ups causes local fracture of the jog and grain boundary sliding opens up the jog to form a microvoid. Chen and Machlin (77) suggested that only grain boundary sliding is needed to open up the jog and generate the grain boundary microvoids. On the other hand, Kikuchi et al. (78) studied the nucleation of grain boundary voids in Astroloy by deforming the sample at room temperature and annealing. They concluded that stress produced by dislocation pile-ups is sufficient to cause decohesion of the boundary and nucleate microvoids. Lim and Raj (43) also observed slip trace impingement induced nucleation of grain boundary voids in nickel during low-cycle fatigue tests. However, in both reports (43,78), TEM two-stage replica techniques were used and grain boundary sliding was not observed in the formation of the voids. Instead, they found that each void was associated with one or two slip lines.

In Chapter 3, Figure 27a and 27b have shown that in the early stage of bubble formation, two sets of bubbles were found on the grain boundary ahead of a main
propagating crack. The spacing between those larger bubbles (indicated by 'A') were around 0.2μm, which was comparable to the spacings of slip lines observed in Figure 28. Thus it was very likely that the formation of the larger bubbles in Figure 27b was aided by the slip line impingement on the grain boundary.

In Figure 28, several slip lines impinging on the grain boundary are shown. Each slip line consists of a number of dislocations on a same slip plane. Those dislocations were generated by dislocation sources inside the grain. Dislocation pile-ups formed as they encountered a barrier such as the grain boundary. Because of plastic incompatibility, the pile-up produced a stress concentration at the grain boundary. The force acting on the leading dislocation is proportional to the external stress and the number of the dislocations in the pile-up (79). For a pile-up consisting of large number of dislocations, the stress concentration is so high that some accommodation must occur to relax it. One way is to generate nonparallel slip systems in the next grain, another is to form a crack nucleus on the grain boundary. For boundaries with large misorientations, the former process is difficult and before it occurs, some voids could already form at the impingement. Lim and Raj (80) studied the effects of grain boundary misorientations on the slip-induced cavitation in nickel at elevated temperatures, and concluded that it was easier to form
voids at high \( \Sigma \) grain boundaries. A similar situation could occur in the IGSCC of Alloy 600. The void nuclei could be initiated by the high stress exerted by the dislocation pile-ups on the grain boundaries.

The replica shown in Figure 28 was taken immediately after the specimen was bent at room temperature. No microvoids were formed due to the lack of the assistance from the high methane pressure. However, in the stress corrosion test, specimens were deformed at an appreciably higher temperature (380 K higher) in a hydrogen-containing environment. The void nucleation may be aided by the formation of high methane pressure inside the voids. A higher temperature also increases the rate of diffusion. The voids could grow up to a visible size in the TEM by removing nickel atoms from the void surface through boundary diffusion.

Shen and Shewmon (42) have shown that homogeneous nucleation of bubbles is possible. In their analysis, the homogeneous nucleation was aided by:

1. high methane pressure in the void embryo and normal stress exerted on the grain boundary,

2. reduced surface energy of nucleating crack from hydrogen chemisorption, which in turn, decreased the void tip angle and the required nucleation barrier,

3. the slip impingement on the grain boundary.

In contrast, the present study showed that the nucleation of the first set of bubbles were induced by the slip
impingement on the grain boundary. It indicated the nucleation of bubbles could occur in a heterogeneous manner. Nonetheless, some aspects in the analysis by Shen and Shewmon still apply in the present discussion. At the test temperature of 300-400°C, hydrogen generated by corrosion could adsorb on the surface and diffuse into the metal to react with carbon to form methane. A high fugacity of methane can be produced through reaction 4.1 (81), and the equilibrium methane fugacity can be calculated from the equilibrium constant.

\[ 2\text{H}_2 + \text{C} \rightarrow \text{CH}_4 \]  
\[ f_m = 1.6 \times 10^{-6} a_C (f_{\text{H}_2})^2 \exp(13670/T) \]

where \( f_m \) is the methane fugacity (in MPa) and \( a_C \) is the carbon activity. After the calculation of the methane fugacity, methane pressure (\( P_m \)) can be calculated from an equation of state derived by Odette and Vagarali (81), which is shown in equation (4.2).

\[ f_m = P_m \exp[C(T)P_m] \]

where \( C(T) \) is a parameter dictated by the magnitude of the methane fugacity and temperature.

\[ C(T) = \begin{cases} 
2.375/T + 1.1776 \times 10^{-3} \text{ MPa}^{-1} & f > 10^4 \text{ MPa} \\
1.1875/T + 3.0888 \times 10^{-3} \text{ MPa}^{-1} & f = 10^3-10^4 \text{ MPa} \\
0.005 \text{ MPa}^{-1} & f < 10^3 \text{ MPa}
\end{cases} \]

To calculate the equilibrium methane fugacity, we have to know the hydrogen pressure in the environment and the carbon activity in the alloy. High fugacity of hydrogen can be generated by reacting clean metal with water. Take
chromium as an example,

\[
\frac{2}{3} \text{Cr} + \frac{1}{3} \text{H}_2\text{O} = \frac{1}{3} \text{Cr}_2\text{O}_3 + \text{H}_2 \tag{4.4}
\]

\[\Delta G^\circ = -25000 \text{ cal/mol (400°C)}\]

If \(a_c = 0.1\), the ratio of \(\text{H}_2/\text{H}_2\text{O}\) at equilibrium would reach \(3 \times 10^7\). Although the number of \(\text{H}\) atoms adsorbed on the metal surface and the amount of released \(\text{H}_2\) are not known, the ratio suggests that extremely high fugacities of hydrogen in the metal just beneath the reacting surface are possible. U-bend specimens tested in dry hydrogen at 27 MPa at 400°C were not cracked but the same specimen tested in 380°C deaerated steam cracked in 339 hours. Thus the hydrogen fugacity is taken as 5 times of the dry hydrogen pressure, or 135 MPa. Carbon activity was estimated by Shen and Shewmon (42) as 0.1 that of graphite. Using equation 4.2 and 4.3, the methane pressure at 380°C is estimated at 1600 MPa. Nonideality of methane gas gives non-sensitivity of methane pressure with the hydrogen fugacity. Even if the hydrogen fugacity were 270 MPa, the methane pressure would only increase another 400 MPa. Thus the methane pressure at 1600 MPa would be a fair estimate. Shen and Shewmon (42) proposed that hydrogen chemisorption reduces the surface energy of nucleating cracks and decreases the required combination of methane pressure and normal stress to 1300 MPa for the nucleation. The methane pressure developed inside the nucleating voids exceeds the value. This indicates that the void nucleus formed by the slip impingement can be
stabilized with the aid of high methane pressure.

In IGSCC of U-bend specimens (8), the observation of general surface cracking on all the grain boundaries suggests that in the nucleation stage the orientation of grain boundaries to the loading axis is not important. This fits the discussion that the void nucleation is aided by the high pressure methane gas inside the voids. The role of the load in the nucleation of the first set of bubbles is to introduce plastic strain, or slip which induces void nucleus at the impingement on the grain boundary. In the next section, the nucleation of the second set of grain boundary bubbles is discussed.

4.1.2 NUCLEATION OF THE SECOND SET OF GRAIN BOUNDARY METHANE BUBBLES

The high methane pressure inside the nucleating bubbles drives atoms from the void surface into the boundary to exert a stress on the matrix normal to the boundary. To achieve local equilibrium at the junction of the bubble-boundary interface, the stress would be equal to the methane pressure inside the bubble. Removing atoms into the grain boundary is the same as moving vacancies into the bubble, which increase the bubble volume and allow methane gas to do work. This decreases the chemical potential of vacancies near the bubble surface by an amount of methane pressure less the sintering force times the atomic volume, or \( (P_m - 2\gamma/a)\Omega \) per vacancy. The
sintering force is expressed by $2\gamma/a$, where $\gamma$ is the surface energy of the bubble and $a$ is the bubble radius. $\Omega$ is the atomic volume which is roughly equal to the vacancy volume of the vacancy. To a distance farther from the bubble the chemical potential remains unchanged. The difference in chemical potential drives the diffusion of vacancies into the bubble. At the testing temperature range (300-400°C), grain boundary diffusion is rapid, thus the removal of atoms from the void nucleus follows the path along grain boundary.

Raj and Ashby (44) and Raj, Shih and Johnson (45) first studied the cavitation on the grain boundary at elevated temperatures. From a similar approach Shewmon (82) considered the effect of internal methane pressure inside the voids in the case of hydrogen attack in steels. This problem was also studied by Parthasarathy (74) and Shewmon (75). In all studies, a periodic array of voids is assumed on the plane of grain boundary. The voids grow by boundary diffusion of atoms from void surfaces to the boundary. Assuming constant boundary thickness, it was treated as a cylindrical problem around each void. At steady state, there is no net accumulation of material in any part of the boundary. Thus the expansion rate of the void must equal to the flux of atoms removed from the voids, which gives a differential equation of the chemical potential gradient and the void expansion rate. Enforcing mechanical equilibrium among the voids and boundary, the
chemical potential gradient was obtained, which induces stress field between the bubbles.

Parthasarathy (74) and Shewmon (75) have shown that for diffusion controlled growth of bubbles, at steady state the stress distribution between two bubbles would be:

\[\sigma(r) = -B(P_m + \sigma_a - \frac{2\gamma}{a}) \left( \frac{r^2 - a^2}{2} - \frac{b^2 \ln \frac{a}{r}}{2} \right) - \frac{2\gamma}{a} \]  

\[B = \frac{1}{b^2 \left[ x^2 \left( 1 - x^2/4 \right) - \ln(x) - 3/4 \right]}\]  

where \(\sigma_a\) is the average stress normal to the boundary, \(r\) is the radial distance from the bubble, \(a\) is bubble radius, \(b\) is the half bubble spacing, and \(X = a/b\). For diffusion void growth rate, the rate of void growth equals to the rate of atoms added to the grain boundary. The void growth rate can be derived form the boundary diffusion processes. Equation 4.6 gives the void growth rate.

\[\frac{dV}{dt} = \frac{2\pi D_b \delta \Omega}{kT} \left( \sigma_a + P_m - \frac{2\gamma}{a} \right) \left[ \frac{(1-x^2)^2}{x^2 \left( 1 - x^2/4 \right) - 3/4 \ln x} \right] \]  

where \(\delta\) is the grain boundary thickness and \(V\) is the bubble volume. In equation 4.6, the net driving force for the bubble growth is \((\sigma_a + P_m - 2\gamma/a)\). This result becomes clear that the effect of internal pressure inside the void is exactly the same as the effect of stress normal to the boundary.

In Figure 72, Shewmon (75) shows the steady-state stress distribution between two grain boundary bubbles when the specimen is undergoing hydrogen attack in the
absence of applied stress. It is seen from the plot that high compressive stress develops just next to the junction of bubble-boundary interface. This can be understood as wedging atoms into the grain boundary thus exerting a stress until it equal to the methane pressure inside the bubble (82). Tensile stress forms ahead of the wedge even without the applied stress. At steady-state, the magnitude of the tensile stress is determined by the methane pressure and the ratio of bubble size to bubble spacing, which is indicated in equation 4.5. Maximum tensile stress arises at the center between two bubbles. For a large bubble or a small bubble spacing, such as 0.2\(\mu\)m or less in the IGSCC of Alloy 600, the stress is higher. This high tensile stress can further aid the nucleation of new bubbles at the region between two growing bubbles.

In Figure 27b several smaller bubbles (indicated by 'B') were observed between those larger 'A' bubbles. These small bubbles were nucleated in the center high tensile region between earlier formed bubbles. Nucleating new bubbles near existing bubbles was also observed in carbon steels by Wang et al. (83) and discussed by Parthasarathy (84). Parallel to the analysis by Parthasarathy, the nucleation of the second set of bubbles in the present study can be discussed as following. From equation 4.5, the magnitude of the stress could reach 0.31 of the methane pressure for a bubble size to spacing ratio
Figure 72. Steady state stress distribution between two grain boundary bubbles. (75)
of 0.25 (in Figure 27b, \(a/b=0.25\)). Taking the methane pressure as 1600 MPa, the maximum stress at the center between two bubbles would equal to 500 MPa. Furthermore, the applied normal stress increases the maximum stress even more, and the normal stress \(\sigma_n\) is included in the first term of equation 4.5. This adds another \(1.31\sigma_n\) into the maximum stress. The stress normal to the void nucleating grain boundary was taken as the average between yield and the ultimate stress (9), or 560 MPa. Thus in steady state, the maximum tensile stress could reach 1240 MPa. The estimated value of maximum stress is very close to the required stress (1300 MPa) for the nucleation of new bubbles (42). Moreover, in transient state, the stress induced by the methane pressure could be even higher next to the bubble-boundary interface before the steep chemical potential gradient is smoothed out by diffusion. Thus the maximum tensile stress could easily exceed 1500 MPa, which further assists the nucleation process.

The nucleation rate of grain boundary cavities at elevated temperatures can be estimated by the number of supercritical nuclei times the probability of finding a vacancy at the perimeter of the critical nucleus (44,85). This can be expressed by equation 4.7.
\[ n = n_0 \exp\left(\frac{-\Delta G^*}{kT}\right) \]  

\[ n_0 = \frac{4\pi\alpha_0^2\gamma D_0^6}{\sigma_n\Omega^{4/3}} \exp\left[\frac{\sigma_n\Omega}{kT}\right] \]  

\[ \Delta G^* = \frac{4\gamma^3 \theta^2 g(\theta)}{3(P_m+\sigma_n)^2} \]

where \( \Delta G^* \) is the free energy change of the void at its critical size, \( \gamma \) is the surface energy, \( g(\theta) \) is a geometry function of the void, \( \theta \) is the dihedral half angle at the apex of the cavity, \( \sigma_n \), and \( P_m \) have been defined previously. In this equation, the nucleation is proceeded by grain boundary diffusion of atoms away from the nucleating voids, and it shows the void nucleation is a very strong function of the normal stress on the boundary and the methane pressure inside the embryo. Thus the previous estimation of 1500 MPa maximum tensile stress can greatly enhance the nucleation process. In Figure 27b, the occurrence of new bubbles was in the region midway between two bubbles, which is consistent with the highest tensile stress developed region. Since boundaries with normal stress have additional contribution to the nucleation rate, the nucleation of the second set of bubbles occurs more readily at boundaries normal to the applied external stress. This is one of the reasons that the final cracking always follows the grain boundaries perpendicular to the applied load.

The model of the nucleation of the two sets of bubbles in IGSCC of Alloy 600 is supported by the
observation of the same spacing between slip lines and that of early formed bubbles and the occurrence of small bubbles nucleated in the high tensile stress region between methane bubbles. The nucleation of the first set of bubbles is aided by slip line impingement, and the nucleation of the second set of bubbles is assisted by the tensile stress induced by methane pressure and the applied stress.

4.2 IGSCC OF ALLOY X-750 IN HIGH TEMPERATURE DEAERATED WATER

The discussion in this Section will show that the IGSCC in Alloy X-750 is the same as that in Alloy 600, and the IGSCC of X-750 fits the hydrogen induced void-linkage mechanism.

From the results in Sections 3.2.1 through 3.2.4, the observation of the IGSCC in high temperature deaerated water and the microstructure of Alloy X-750 can be summarized as follows:

(1). The most IGSCC susceptible heat treatment was the two-stage aging. The one-stage aged specimens were much more resistant to the IGSCC than that of two-stage aged.

(2). Plenty of grain boundary chromium carbides were observed in the one-stage aged samples, while grain boundaries of the two-stage aged samples were relatively free of chromium carbides.
(3). Microvoids formed in the IGSCC crack were directly observed by the SEM and TEM.

(4). Cracks initiated at the outer side of the U-bend where the tensile stress and strain were the highest.

(5). The final fracture occurred on a plane normal to the applied tensile stress, and surface cracks normal to the stress were wider than the others, indicating that the crack growth was enhanced by the tensile stress normal to the boundary.

These characteristics suggested that the IGSCC of Alloy X-750 in high temperature deaerated water was the same as that observed in Alloy 600, and the hydrogen induced void-linkage model also applied in this case.

Thus the IGSCC in Alloy X-750 started from the nucleation of microvoids on the grain boundaries, which was assisted by high pressures methane gas formed by the reaction of corrosion generated hydrogen and carbon in solution. The combination of the tensile stress normal to the boundary and the methane pressure then drove the growth of the voids. Finally the voids joined to form the fissures.

The validity of the model was checked in the SEM and TEM. In Figure 42a, numerous surface cracks were found on the specimen surface. Discrete microvoids and linked voids were observed inside the surface cracks (Figures 42b, 45), as well as fine cracks near a main crack (Figure 43b). These evidences suggest that the IGSCC was caused by the formation and link up of grain boundary voids.
The difference in the IGSCC susceptibility of the two differently aged samples stemmed from the difference in the existence/absence of the grain boundary chromium carbides. Since for two-stage aged samples, no chromium carbides were formed on the grain boundary, the material contained more carbon in solution near the grain boundary. Hence high pressure methane gas could be formed, which assisted the nucleation of the grain boundary microvoids.

In contrast, in one-stage aged material, many grain boundaries were covered by discontinuously precipitated chromium carbides. Parallel to an analysis in Alloy 600 by Shen (9), the carbon activity in the matrix near the grain boundary with chromium carbide would decrease by a factor of 30 ($8^{6}$). This drastically retards the nucleation of the IGSCC but not enough to stop it. This explains why the crack growth rates in the one-stage aged U-bend specimen was one order of magnitude slower than that of the two-stage aged samples.

The tensile stress normal to the grain boundary was essential in the growth stage of the IGSCC crack in Alloy X-750, based on the observations of (4) and (5) in the first paragraph of this section. In the void growth stage, the formation of methane quickly drains the carbon in the surrounding region near the boundary so that the equilibrium methane pressure rapidly dropped. As discussed in Section 4.2, the tensile stress is important in this stage because it is the major force driving the
diffusion of atom away for the void growth. Moreover, the nucleation of voids could be assisted by the slip line impingement on the grain boundary. Thus the IGSCC always occurred right at the top of the bend where both the stress and plastic deformation were the highest.

The solution annealed U-bend sample did not crack in the test because the applied stress was not high enough to drive any void growth. Since the specimen was not age hardened, the strength of the material was low, which is reflected by the low hardness of the specimen ($R_B$ 82 compared to $R_C$ 35 of the aged specimens). During the preparation of the U-bend, the specimen was easily deformed plastically and the stress left on the specimen was not much. In the void growth stage, the tensile stress normal to the grain boundary is necessary to drive the diffusion of atoms away from the void. For the solution annealed specimens, although the plastic deformation was enough to produce sufficient amount of slip for the void nucleation, the low applied stress made the growth of voids extremely difficult. This was why the solution annealed specimen did not fail in the U-bend test. However, if the external tensile stress was high, the void growth could be assisted and the IGSCC would occur in the solution annealed specimen. In an unpublished work done by Xia et al. (87), the same solution annealed specimen showed the IGSCC failure in the slow strain rate test (SSRT) after 122 hours exposure in
the simulated PWR water at 350°C. The fracture surface shows the same fracture as the IGSCC in the two-stage aged specimens in the present study. Since the applied stress in the SSRT test was higher than that of the U-bend test, the void growth in this test was much easier than the latter.

From the discussion in this section, it is clear that the hydrogen induced void linkage model fits the cracking mechanism for the IGSCC in Alloy X-750 in high temperature deaerated water.

4.3 ACTIVATION ENERGY AND STRESS INTENSITY DEPENDENCY ON IGSCC CRACK GROWTH RATES IN ALLOY 600 AND X-750

The discussion for the crack growth studies on the IGSCC of Alloy 600 in this Section will address the following questions:
1. How was the crack growth rate assisted by the stress intensity?
2. Why the activation energy of the IGSCC is strongly $K_I$ dependent?
3. What determines the exponent of the stress intensity dependence on the crack growth rates?

From the study of crack growth in Alloy 600 MWOL specimens, the characteristics of the IGSCC can be summarized as follows:
- At a same temperature, crack growth rates were higher for higher applied stress intensity.

- A higher stress intensity gives lower apparent activation energy, whereas a lower $K_I$ gives higher apparent activation energy.

- Assuming $da/dt=AK_I^n$, the exponent $n$ was close to 7 at low temperatures, while $n$ was 1.7 for high temperature.

As discussed in the previous sections, the stress assists both the nucleation and the growth of the microvoids. In the meantime, the stress introduced a plastic zone ahead of the crack tip. The plastic zone size $r_p$ can be estimated for the plane strain condition by (88):

$$r_p = \frac{K_I^2}{6 \pi \sigma_y^2}$$

where the $\sigma_y$ is the yield stress. In the present study, $K_I=60$ MPa$\sqrt{m}$ and $\sigma_y=305$ MPa, the plastic zone $r_p$ was estimated to be around 2000 $\mu$m. For the higher stress intensity, the zone would be even larger. Since the IGSCC in Alloy 600 occurs within two grains diameter (about 50 $\mu$m) from a main crack tip, all the nucleation and growth of the microvoids would take place well within the plastic zone. Thus the discussion is based on what occurs inside the plastic zone.

Increasing the stress intensity gave higher stress exerted on the specimen and a larger plastic zone. As indicated in Section 4.1, the first stage of bubble
nucleation is aided by the impingement of slip lines on the grain boundary. A higher applied stress produces more plastic deformation which increases the amount of slip and increases nucleation sites for the void nucleation on the grain boundary. Moreover, a higher stress increases the high tensile stress between two earlier formed bubbles, which enhances the second stage of nucleation. Thus the high stress gives tremendous effects on the nucleation of voids.

In the growth stage, the tensile stress normal to the boundary enhances the crack propagation by stress assisted grain boundary diffusion. The driving force to inject atoms into the boundary increases due to the high magnitude of chemical potential difference between the bubble and the region farther away. Thus the diffusion of atoms increases and crack grows faster. In this stage, the normal stress on the boundary was the major driving force for the growth of the bubbles.

As shown in 3.1.2., Plotting \( \ln(da/dt) \) versus \( 1/T \), a linear relationship was obtained, and the slope gave the apparent activation energy for the cracking process. The activation energies were 80 kJ/mol and 168 kJ/mol for initial \( K_I = 80 \text{ MPa}\sqrt{m} \) and 60 MPa\( \sqrt{m} \), respectively. The stress intensity is a function of stress and crack-length \( (a/W) \), where \( W \) is the specimen width. Since the crack growth rates were very slow in the present studies, the \( (a/W) \) did not change much during the tests. The change in
$K_I$ was caused by the change in the applied stress. The two values of the activation energy came from the difference in the stress on the specimens.

Kinetically, the activation energy correspond to the rate controlling step in the reaction process. The activation energy of the IGSCC in Alloy 600 can be expressed by:

$$\frac{da}{dt} = A \exp\left(-\frac{Q_{app}}{RT}\right) \quad (4.9)$$

where $Q_{app}$ is the activation energies for the IGSCC process. The IGSCC in Alloy 600 includes a continuous nucleation process ahead of the crack tip and the growth of voids. If the crack growth is void growth controlled, the activation energy $Q_{app}$ should equal to the activation energy of the boundary diffusion of the nickel atoms. This case would be similar to the hydrogen attack of steels where the iron boundary diffusion is the rate controlling step (82).

In the high stress intensity case, the void nucleation rate was high, and the IGSCC was limited by the rate of void growth as previously discussed. For $K_I=80$ MPa√m, Shen (9) has shown that the measured activation energy fit the activation energy of the boundary diffusion of the nickel atoms in Alloy 600, indicating the boundary diffusion was the rate limiting step for the crack growth in the IGSCC.
On the other hand, if the bubble nucleation is the controlling process, the crack growth rate can be limited through the variation of the bubble spacing. Integration of equation 4.6 gives the time to fracture for the link-up of voids, which is shown in equation 1.1.

\[ t_f = \frac{0.012kT(2b)^3h(\theta)}{D_b\delta\Omega(P+\sigma_n)} \]  

(1.1)

This equation indicates that the crack growth rate is strongly dependent on the void spacing. The void spacing \(2b\) can easily be changed by the rate of void nucleation. The question now is whether the void spacing has an exponential relationship with the temperature, and how does it change with the applied stress?

In Section 4.1, we have shown that two sets of methane bubbles were nucleated on the grain boundaries in the early stage of the IGSCC of Alloy 600. The first set of bubbles were formed by the impingement of slip lines on the grain boundaries. These bubbles would be readily nucleated by the assistance of the internal high pressure methane gas. The second set of bubbles were formed by homogeneous nucleation process with the assistance of high tensile stress between existing bubbles. Equation 4.7 shows that the void nucleation rate, which depends exponentially on the temperature. \(\Delta G^*\) is the free energy for the formation of a critical sized cavity.
\begin{equation}
\Delta G^* = \frac{4y^3 \theta^2 g(\theta)}{3(P_m+\sigma_n)^2} \tag{4.7}
\end{equation}

For the low stress intensity tests, the stress normal to the cavitated grain boundary was low. Since \(\Delta G^*\) is inversely proportional to the second power of the normal stress plus methane pressure, the decrease in the applied stress would greatly increase the free energy needed to stabilize a critical void nucleus. Thus, the nucleation rate was drastically reduced. In this case, the nucleation of the second set of bubbles was the slowest step in the cracking process, and the apparent IGSCC activation energy \(Q_{\text{app}}\) would be the free energy \(\Delta G^*\) of the nucleation of the second set of bubbles. This explains why the activation energy increased by the decrease of the applied stress on the specimen.

In the study of the IGSCC of Alloy 600, the activation energy was 168 kJ/mol for lower stress intensity experiments. To estimate the \(\Delta G^*\) for the nucleation process, \(y\) and \(\theta\) must be known. If hydrogen chemisorption reduces the surface energy to 0.75 J/m² (one half of the value on a clean Ni surface), \(\theta\) is then equal to 55°. Assuming different values of \((P_m+\sigma_n)\), \(\Delta G^*\) could be calculated. \(\Delta G^*\) is calculated to be 69, 173 and 243 kJ/mol for \((P_m+\sigma_n)\) equals to 1500, 950, and 800 MPa, respectively. Clearly, a higher stress would decrease the
free energy for the nucleation process. This fits the observation of the activation energies in this study.

The reported activation energies for the IGSCC in the PWR environment or the high temperature deaerated water were scattered from 74 to 168 kJ/mol (2,22,24). From the present studies, the activation energy was strongly stress intensity dependent. One possible factor for the variation is the stresses on the specimens were different in different tests.

Figure 73 shows a typical feature of the $K_I$ dependence of the crack growth in stress corrosion tests, in which three distinct regions can be found. Stage 1 and 3 are strongly $K_I$ dependent, and stage 2 is relatively $K_I$ insensitive. In the stress corrosion tests, stage 1 and 2 are commonly observed. The stage 3 denotes the highest applied $K_I$ region, where fast unstable crack growth dominates, and at the end of stage 3 is the critical stress intensity, $K_{IC}$. To the other end, the minimum stress intensity for a measurable crack growth is the threshold stress intensity $K_I$, or $K_{ISCC}$, where the subscript I indicated mode I loading. For testing the crack growth rates on different $K_I$ at the same temperature, the relationship between crack growth rate and $K_I$ could be expressed by $da/dt=AK_I^n$. The exponent $n$ indicated the $K_I$ dependence.

In the present study, the exponents seemed to vary in a large scale from low temperature to high temperatures.
Figure 73. Typical diagram of the K dependence on the crack growth rate in stress corrosion test.
Since only two $K_I$ values were used in the tests, it is difficult to tell if all the experiments were in the stage 2 growth. Especially for lower temperature, it is likely that the low $K_I$ cases the crack growth was in the stage 1, and the calculated exponent $n$ would be misleading. At the highest temperature (380°C), it is reasonable to believe that both low and high $K_I$ tests were performed in stage 2 growth and the estimation for $n$ would be reliable. In this case, the exponent $n$ is 1.7. According to the analysis by Raj and Baik (89), $K_I$ has a second power dependence to the crack growth rate if the cavity growth ahead of the main crack is grain boundary diffusion controlled. Here the $K_I$ exponent is 1.7 which is close to the value for diffusion controlled cavity growth.

At lower temperatures, $K_I$ dependencies were higher. The exponent $n$ was 4.5 at 360°C, and close to 7 at 340 and 320°C. Such high stress intensity dependencies are not commonly observed in stage 2. One possible reason is the low $K_I$ ($K=60$MPa\(\sqrt{m}\)) experiments at these temperatures were tested in the stage 1 growth, and the calculated $n$ values includes the transition from the stage 2 to the stage 1 dependencies. In stage 1, the nucleation of void dominated the cracking process. If the nucleation of methane bubbles was rate limiting in the stage 1 growth, the stress would have a strong effect on the crack growth rates.
In Alloy X-750, the activation energies were 86, 116, and 212 kJ/mol, for the initial stress intensities of 60.8, 32.2, and 15.4 MPa\(\sqrt{m}\), respectively. These indicate that a low applied stress intensity gave a high activation energy, and a high stress intensity decreased the activation energy. Also, the crack growth rates increased with the stress intensity and temperature. These characteristics of the IGSCC crack growth were completely the same as that of the Alloy 600. Hence, the above discussion also applies to the Alloy X-750.

4.4 IGSCC OF 410SS IN HIGH TEMPERATURE DEAERATED WATER AND ROOM TEMPERATURE TEMPER EMBRITTLEMENT OF 410SS

In Chapter III, the results show the similarity between the IGSCC of 410SS in high temperature water and the temper embrittlement at room temperature. The following discussion will show that the IGSCC in 410SS could stem from the same mechanism as the temper embrittlement.

Table 12 shows that the tempering temperature for IGSCC susceptible material matches the low toughness trough of temper embrittlement in 410SS (Section 1.6.3). One would ask whether the failure modes of the IGSCC and temper embrittlement were really the same phenomena? Examining fracture surfaces of these two types of failure under SEM, several similarities could be found between them. The SEM studies of the fracture surface of IGSCC
cracking are given in Figure 66-68, and the fracture surface of temper embrittlement are given in Figure 69-70. The IGSCC fracture of the 550°C tempered material shows that the fracture initiated as grain boundary cracking and grew into the interior of the specimen during the test. However, over 80% of the surface showed transgranular fracture. Since no corrosion product could be found on the transgranular fracture surface, the fracture surface was freshly opened and was produced by the final overloading break of the specimen.

On the other hand, the fracture surface of temper embrittlement of 410SS showed almost the exact characteristics as the IGSCC fracture surfaces. The tension side of the bend revealed several sites of intergranular cracking, and the rest of the surface showed the transgranular fracture by the overloading.

The similarities of those two types of fracture indicated that tempering at 400-600°C would intrinsically weaken the grain boundary and assist the initiation of IGSCC in 410SS. A bending process in the preparation of U-bend specimens for stress corrosion test probably had already generated some initiation of grain boundary fracture. The following testing in the high temperature water would propagate the pre-existing crack on the tension side of the specimen. The succeeding propagation of the crack in the corrosion environment could be assisted both by anodic dissolution or hydrogen embrittlement.
The hydrogen could be produced in the corrosion process, then diffused into the metal and embrittled the metal. Hydrogen embrittlement is an important mechanism for stress corrosion in high strength steel such as 410SS (Section 1.6.2). But the crack path would not necessarily follow the grain boundary, unless the grain boundaries were already weakened. The formation of the grain boundary methane bubbles could be a possible grain boundary weakening mechanism. However, the observation of grain boundary chromium carbides in 550°C tempered specimen opposes this argument. Grain boundary chromium carbides would decrease the IGSCC susceptibility of the specimen, such as that occurred in the thermally treated Alloy 600 and one-stage aged Alloy X-750. The observation of the IGSCC in the 550°C tempered 410SS conflicted the methane formation mechanism. Another possible mechanism that weaken the grain boundary was the impurity segregation.

Lemble et al. (59) reported that phosphorus segregation on the grain boundary of 12%Cr martensitic steel is the main cause for the intergranular fracture for a specimen tempered at 550°C (Section 1.6.3.2). The 410SS sheet used in the present study contains 0.022% phosphorus, which is high enough to make the phosphorus segregation a possible weakening mechanism to the grain mechanism. Specimens tempered at 450 and 500°C were bent broken at room temperature and examined under SEM, where
numerous grain boundary cracks were observed. This suggested that the grain boundaries of these samples were intrinsically very weak. Intergranular cracks on the fracture surface shows very clean and smooth grain facet, which was a typical fracture surface caused by impurity segregation (60,61). No grain boundary precipitates or inclusions could be observed on the facets. Thus impurity segregation on the grain boundary is a strong candidate for the temper embrittlement as well as the IGSCC of the 410SS.
CHAPTER V

CONCLUSIONS

5.1 NUCLEATION AND GROWTH OF BUBBLES IN THE IGSCC OF ALLOY 600 HIGH TEMPERATURE DEAERATED WATER

1. The slip line spacing was the same as the bubble spacing for the nucleation of the first set of bubbles. This indicated that the nucleation of the first set of bubbles were assisted by the slip impingement on the grain boundary. The high pressure methane gas inside the bubble nuclei also aided the bubble nucleation.

2. Smaller bubbles between the first set of bubbles were formed by the assistance of the tensile stress normal to the boundary.

3. The growth of bubbles was aided by the tensile stress normal to the boundary.

4. TEM replicas confirmed the IGSCC of Alloy 600 was caused by the hydrogen induced void-linkage mechanism.
5.2 ACTIVATION ENERGY AND STRESS INTENSITY DEPENDENCY ON IGSCC CRACK GROWTH RATES OF ALLOY 600

1. The apparent activation energy for the initial $K_I = 60$ MPa/$\sqrt{m}$ in the IGSCC crack growth studies was 168 kJ/mol.

2. The activation energy was strongly stress intensity dependent for the low $K_I$ tests, suggesting the nucleation of bubbles might be the rate limiting step in the IGSCC failure.

3. The stress intensity exponent was 1.7 for the specimen tested at 380°C, indicating the void growth was diffusion controlled.

5.3 IGSCC OF ALLOY X-750

1. The most IGSCC susceptible heat treatment was the two-stage aging. The one-stage aged specimens were much more resistant to the IGSCC than that of the two-stage aged. The IGSCC crack growth rate of the two-stage aged specimens were one order of magnitude faster than that of the one-stage aged.

2. Plenty of grain boundary chromium carbides were observed in the one-stage aged samples, while grain boundaries of the two-stage aged samples were relatively free of chromium carbides.

3. Microvoids formed in the IGSCC crack were directly observed by the SEM and TEM.

4. Cracks initiated at the outer side of the U-bend where the tensile stress and strain were the highest.
5. The final fracture occurred on a plane normal to the applied tensile stress. Surface cracks normal to the stress were wider than the others, indicating that the crack growth was enhanced by the tensile stress normal to the boundary.

6. The IGSCC of Alloy X-750 was caused by the hydrogen induced void-linkage mechanism. It was produced by the formation and growth of the methane bubbles on the grain boundary.

7. In the crack growth rate studies of the MWOL specimen, three activation energies were obtained. The activation energies were 86, 116, and 212 kJ/mol for $K_I=60.8$, 32.2, 15.4 MPa/m, respectively.

5.4 IGSCC OF 410SS IN HIGH TEMPERATURE DEAERATED WATER AND ROOM TEMPERATURE TEMPER EMBRITTLEMENT OF 410SS

1. Specimens tempered at 550°C for two hours showed the highest IGSCC susceptibility in high temperature deaerated water.

2. IGSCC occurred for specimens tempered at 500 and 550°C. Both their hardness were greater than $R_C$ 26.

3. Temper embrittlement of specimens were observed by tempering at 450 and 550°C for two hours.

4. The fracture surfaces of the IGSCC failure and the temper embrittlement showed several similarities, indicating the IGSCC could be caused by the temper embrittlement.
APPENDIX A

RELATIONSHIP BETWEEN CRACK LENGTH, BACK-FACE STRAIN, AND LOAD FOR MWOL SPECIMEN (9)

The experimental results of MWOL specimens using back-face strain technique (69) can be expressed by

\[(BFS) = A(a/W)P\]  \hspace{1cm} (A-1)

where BFS is the magnitude of back-face strain, P is load, and A(a/W) is a function of a/W.

With the normalizing parameter

\[P^* = P/BWE\]  \hspace{1cm} (A-2)

where B is the specimen thickness, W its width, and E is Young's modulus, then

\[(BFS) = A^*(a/W)P^*\]  \hspace{1cm} (A-3)

where A^*(a/W) is a function of a/W. Thus

\[A^*(a/W) = [(BFS)/P]BWE\]  \hspace{1cm} (A-4)

Normalized in this way, A^*(a/W) is independent of specimen dimensions and material for the MWOL geometries.

Therefore, from Equation A-4, the load can be determined for any specimen size and thickness and for any value of E, if A^*(a/W) and BFS are known. Values of A^* as a function of a/W are given in TABLE A-1 (69). BFS and a/W can be measured experimentally.

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\[ A^{*}(a/W) = \left[ \frac{\text{BFS}}{P} \right] \frac{B}{W} E, \text{ m/m} \]

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<tr>
<th>a/W</th>
<th>MWOL Specimen</th>
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<tr>
<td>0.31</td>
<td>3.49</td>
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<tr>
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APPENDIX B

CALCULATION OF $K_I$ (9)

The following equations based on boundary co-location values determined for MWOL specimen can be used to calculate the stress intensity factor ($K_I$) as long as the specimen half-height to width ratio ($H/W$) is 0.486 (70).

$$K_I = \frac{P (2 + a/W)}{B W^{1/2} (1 - a/W)^{1/2}} \left[1.308 + 5.287(a/W)^2 - 19.67(a/W)^3 + 24.57(a/W)^4 - 10.27(a/W)^5\right]^{-1/2}$$

$$2V_{LL} = \frac{P}{E B} \exp[f(a/W)]$$

$$f(a/W) = [1.623 + 3.352(a/W) + 8.205(a/W)^2 - 19.57(a/W)^3 + 15.23(a/W)^4]$$

where $B$ is the specimen thickness, $W$ its width, $P$ is load, $a$ is the crack length, and $2V_{LL}$ is the total crack mouth opening displacement at the load line. The polynomial regression equation agrees with experimentally determined co-location values within 1% for $0.2 \leq a/W \leq 0.95$.

For a specimen loaded with a rigid loading device, which means $2V_{LL}$ in Equation B-2 is a constant as the load decreases during the test, the in-situ $K_I$ value of the specimen can be directly calculated by using Equation B-1. However, in most cases, the loading device is not rigid.
and $2V_{LL}$ is increased as the load decreases during the test. For the specimens tested in the high temperature solution environment, $2V_{LL}$ cannot be measured directly by the clip gage or any other methods, further calculation (64) is needed to obtain the true $2V_{LL}$ value. If the load decrease of the specimens during the test is very low, then the change of $2V_{LL}$ is very small. Therefore, $2V_{LL}$ can be assumed to be a constant during the test.

Loading is performed at room temperature, however, the load will relax at the test temperatures (260 to 380°C). The exact amount of load relaxation is unknown but the initial load at temperature can be estimated from thermal expansion coefficient (TEC) data. The material (Alloy 718) of the loading devices (bolt and tup) has almost the same TEC (about $14.3 \times 10^{-6}$ /°C at 350°C) as the specimen material (Alloy 600). On the other hand, the material (Zr-705) of the insulator (thin disc) has a lower TEC (about $9 \times 10^{-6}$ /°C at 350°C) than that of Alloy 600. This difference reduces $2V_{LL}$ as well as the load of the specimen at the testing temperature. The change in load between room temperature and the operating temperature can be estimated as follows:

1. Using the initial room-temperature load and Young's modulus of the specimen at the operating temperature to compute the $2V_{LL}$ value from Equation B-2 for given $a/W$ and B.

2. Calculate the difference (due to the thermal expansion
effects) between thin disc and specimen. It can be expressed by

\[ d = L \times (\alpha_s - \alpha_D) \times \Delta T \]

where \( L \) is the disc thickness, \( \alpha_s \) is the TEC of specimen, \( \alpha_D \) is the TEC of disc, and \( \Delta T \) is the difference between the testing temperature and room temperature.

3. The actual load before relaxation at the testing temperature can be calculated from Equation B-2 by using the \((2V_{LL} - d)\) value.
APPENDIX C

KLINTWORTH ANALYSIS FOR CONVERTING POTENTIALS TO CRACK LENGTH (9)

The conversion from measured potential values to $a/W$ involves the use of the finite element calculations of Klintworth (71), who presents tabular data for different types of fracture mechanics specimens. His data is in arbitrary units (of voltage) and therefore a conversion from measured potential to the arbitrary Klintworth potential scale is needed. The following procedure is used:

1. Determine the initial crack length. This usually is the depth of a machined notch, which can be very accurately measured. Even if this can only be determined approximately, there will be no serious errors in the relative $a/W$ (i.e. growth of the crack), as can be seen from the very mild curvature to the Klintworth curve (Figure C-1).
2. Set up the test with the probes in the positions previously described in 2.1.3.5 and allow the test conditions to equilibrate (flow rate, temperature,
Figure C-1. Klintworth curve for converting electrical potentials to normalized crack length (71).
etc.

3. Acquire data with the specimen loaded to a reasonably high stress intensity, although not high enough to induce crack growth. This will be the reference data against which further data will be ratioed. Variations in the dc current level or temperature will induce significant errors unless a probe is employed on the back face of the specimen.

4. Once a stable reference value is obtained (averaging over between several hours and one day is recommended), crack growth measurements can proceed. As the crack grows, a higher voltage will be measured on the potential probes.

5. It is now necessary to establish a conversion between the measured potentials and the (arbitrary) potential scale used by Klintworth. This can be done in a simple equality between the measured and Klintworth potentials as the crack grows:

\[
\frac{E_{\text{new, Klintworth}}}{E_{\text{measured}}} = \frac{E_{\text{initial, Klintworth}}}{E_{\text{initial, measured}}} \quad (C-1)
\]

A conversion factor can be computed using the ratio of the two initial values (at the right of the above equation). The initial Klintworth value is obtained by taking the known initial (machined) crack length and determining (using the reverse curve fit of a/W versus
Klintworth potential values) a Klintworth potential. This conversion factor is then applied to the new measured potentials to give a corresponding Klintworth potential.

6. The forward curvefit of Klintworth equations have been curve fit for a standard one inch CT specimen and used for the present study.

The equation for converting from the arbitrary Klintworth potentials \((P)\) to \(a/W\) is:

\[
a/W = A_4 \times P^4 + A_3 \times P^3 + A_2 \times P^2 + A_1 \times P + A_0
\]

where:

\[
A_0 = 0.19901 \quad A_1 = -0.002679 \quad A_2 = 3.0191 \times 10^{-5}
\]

\[
A_3 = -8.08596 \times 10^{-8} \quad A_4 = 7.0873 \times 10^{-11}
\]

The equation for converting from \(a/W\) to the Klintworth potentials \((P)\) is

\[
P = B_4 \times (a/W)^4 + B_3 \times (a/W)^3 + B_2 \times (a/W)^2 + B_1 \times (a/W) + B_0
\]

where:

\[
B_0 = -897.068 \quad B_1 = 9911.73 \quad B_2 = -34035.1
\]

\[
B_3 = 51867.9 \quad B_4 = -27777.7
\]

These equations are slightly altered from the initial Klintworth values to provide better accuracy at \(a/W\) values over 0.55. Since the inaccuracies may result from the contribution of the plastic zone, different materials and loading may affect the accuracy. Over 0.65 accuracy will probably be marginal, unless the potential drop technique is calibrated at high \(a/W\). Accuracy will also be compromised by temperature and current fluctuations as well as by out-of-plane cracks.
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