EFFECT OF OXYGEN POTENTIAL ON HIGH TEMPERATURE CRACK GROWTH IN ALLOY 617

by

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ABSTRACT

The effect of oxygen partial pressure on crack growth rates in Alloy 617 has been studied using both static and fatigue loading at 650°C. Tests were conducted at a constant stress intensity factor, $K$, for static loading conditions or constant $\Delta K$ for fatigue loading using a direct current potential drop measurement system to measure crack length. The oxygen concentration was measured on both the outlet of the test retort as well as in-situ with a probe located directly at the specimen surface. High purity argon gas was used to establish oxygen partial pressures at low as $10^{-22}$ atm while premixed oxygen/argon gases were used to vary the oxygen potential.

For fatigue loading, the crack path was observed to be transgranular with increasing growth rates as the oxygen concentration was increased. A transition oxygen partial pressure of approximately $10^{-5}$ atm was found to exist, at which the fatigue crack growth rates started to increase with increases in oxygen concentration in the environment. Furthermore, fatigue at $R = 0.5$ also showed a slight increase in growth rates when the frequency was decreased from 2 Hz to 0.1 Hz. In contrast, the fracture surfaces resulting from static loading were found to be intergranular and exhibited two different environmental behaviors. At a stress intensity factor of 49.5 MPa$\sqrt{m}$, decreasing the oxygen potential lead to an increase in crack growth rates. However, the static loading crack growth rates 33.0 MPa$\sqrt{m}$ exhibited negligible variation with oxygen potential. Detailed microstructural analysis of fracture surfaces and grain boundaries ahead of crack tips was performed using Auger spectroscopy. The results confirm the formation of chromium oxide in the wake of cracking and provide little or no indication of intergranular oxygen diffusion ahead of the crack. However, the resolution of the Auger spectroscopy results was insufficient for a definitive statement in this regard. The observations in this study most closely relate to dynamic embrittlement process involving short range intergranular oxygen absorption under the presence of stress.
# TABLE OF CONTENTS

1. **INTRODUCTION** ........................................................................................................................................... 11

2. **BACKGROUND** ............................................................................................................................................. 15

   2.1 **TIME DEPENDENT FATIGUE CRACK GROWTH** .......................................................... 15

   2.2 **STATIC EMBRITTLEMENT** ............................................................................................... 19

      2.2.1 **Effect of environment** .......................................................................................... 19

      2.2.2 **Role of microstructure** ......................................................................................... 22

      2.2.3 **Possible mechanisms for oxygen embrittlement** ................................................. 23

      2.2.4 **Differences between static embrittlement and other mechanisms** ................. 24

   2.3 **DYNAMIC EMBRITTLEMENT** ......................................................................................... 25

   2.4 **CRACK TIP EMBRITTLEMENT AND OXIDATION** .................................................... 27

      2.4.1 **Microstructural crack tip observations in IN718 and similar alloys** ....... 28

      2.4.2 **Related high temperature corrosion and oxidations studies** ......................... 30

3. **EXPERIMENTAL PROCEDURES** .............................................................................................................. 33

   3.1 **MATERIALS** .................................................................................................................. 33

   3.2 **CONSTANT ΔK AND K CRACK GROWTH TESTS** ....................................................... 35

      3.2.1 **Experimental Setup** ............................................................................................. 35

      3.2.2 **Mechanical Testing Procedures** ............................................................................. 38

   3.3 **FRACTURE SURFACE AND GRAIN BOUNDARY ANALYSIS** .................................. 38

4. **RESULTS** .......................................................................................................................................................... 40

   4.1 **MICROSTRUCTURE AND GRAIN SIZE** ........................................................................... 40

   4.2 **CRACK GROWTH TESTS** .............................................................................................. 41

      4.2.1 **Constant ΔK Fatigue Crack Growth** ...................................................................... 41

      4.2.2 **Static Loading (constant K) Crack Growth** .......................................................... 52

   4.3 **FRACTOGRAPHY** ............................................................................................................. 54

   4.4 **COMPOSITION AND GRAIN BOUNDARY ANALYSIS** ............................................... 62

      4.4.1 **Results for 617-UK-02: K = 30 MPa√m, P_{O_2} = 9.46x10^{-4} atm (~1000 ppm O_2 in Ar)** ................. 62

      4.4.2 **Results for 617-UK-12, K = 30 MPa√m, P_{O_2} = 4.82x10^{-4} atm (~50 ppm O_2 in Ar)** ................. 72

5. **DISCUSSION** ...................................................................................................................................................... 83

   5.1 **CRACK GROWTH RATE DATA** ......................................................................................... 83

      5.1.1 **Fatigue crack growth at R = 0.1 and R = 0.5** .................................................... 83

      5.1.2 **Static crack growth** .................................................................................................. 87

      5.1.3 **Possible crack tip damage mechanisms** ................................................................. 89

   5.2 **MICROSTRUCTURAL ANALYSIS** ..................................................................................... 92
LIST OF FIGURES

Figure 1. Fatigue life of IN706 as a function of temperature under air and vacuum conditions [4] ....................... 16

Figure 2. Change in fatigue crack growth rate with test frequency and temperature for Alloy 718 at $\Delta K = 40$ MPa$m$ [30]. ......................................................................................................................... 17

Figure 3. Constant $\Delta K$ fatigue crack growth rates as a function of oxygen partial pressure in Alloy 718 [37]. ....... 18

Figure 4. The effect of 200 hr of air and vacuum exposure at 1000°C on the tensile ductility of Ni270 at a variety of temperatures [10]. The two open circles are samples machined from the centers of blanks after vacuum exposure. ............................................................................................................. 20

Figure 5. Fracture surfaces of Ni200 after tensile testing at 800°C, (a) vacuum annealed condition—ductile rupture; (b) air exposed 100 hr at 1000°C—intergranular fracture [8] ................................................................................................................................. 21

Figure 6. The tensile ductility of Hastelloy X as a function of temperature for specimen air exposed (open circles) and vacuum exposed (closed circles) at 1000°C before testing in vacuum [9].................................................. 22

Figure 7. Schematic illustration of the interchange between grain boundary sliding (G.B.S.) and boundary pinning which can lead to embrittlement at intermediate temperature in nickel [10] ................................................................. 24

Figure 8. Schematic illustration of the stress accelerated grain boundary oxidation (SAGBO) and oxygen embrittlement processes. ................................................................................................................... 25

Figure 9. Load relaxation curve resulting from cracking of Alloy 718 in oxygen at 650°C loaded in pure bending at fixed displacement. Note that crack growth was completely arrested when the test chamber was evacuated to below $10^{-5}$ Pa [22] ................................................................................................................. 26

Figure 10. Effect of grain boundary engineering (via thermomechanical processing) on the fixed displacement load-relaxation curves for Alloy 718 at 650°C in air ........................................................................................................... 28

Figure 11. Proposed mechanism for oxide formation in IN718. Note that $t_p$ is the transition time which is the time necessary to form a passive Cr$_2$O$_3$ film and limit oxygen diffusion into the grain boundary [14] ......... 30

Figure 12. C(T) specimen geometry (all dimensions in inches) .................................................................................. 34

Figure 13. Schematic of experimental setup for constant $\Delta K$ and K crack growth tests .................................................................................................................. 36

Figure 14. Schematic illustration of the control of the mechanical testing system employing a DC potential drop technique........................................................................................................................................ 37

Figure 15. Three-dimensional reconstruction of Alloy 617 microstructure at 100x. Surfaces have been electrolytically etched at 8V for 25s in a 7.8% perchloric acid solution. ......................................................................................................................... 40

Figure 16. Comparison of microstructures at 50x magnification in the as-received condition (top) to microstructure after testing for $\sim$750 hr at 650°C (bottom). The long transverse direction is along the x-axis and the rolling direction along the y-axis. ................................................................................................................... 42

Figure 17. Crack length versus the number of cycles showing the transition in crack growth rates in a standard test sequence. Test conditions were $R = 0.1$ and a gas environment of 1000 vppm O$_2$ in argon. ............... 43

Figure 18. Fatigue crack growth rate vs. the stress intensity factor range with $R = 0.1$ and $P_{O_2} < 10^{-12}$ atm .......... 45

Figure 19. Fatigue crack growth rate vs. the stress intensity factor range with $R = 0.1$ and $P_{O_2} = 9.71 \times 10^{-4}$ atm ...... 45

Figure 20. Fatigue crack growth rate vs. the stress intensity factor range with $R = 0.1$ and 0.1 Hz loading .......... 46

Figure 21. Fatigue crack growth rate vs. the stress intensity factor range with $R = 0.1$ and 2 Hz loading .......... 46

Figure 22. Fatigue crack growth rate vs. the stress intensity factor range with $R = 0.5$ and $P_{O_2} < 10^{-21}$ atm .. 48

Figure 23. Fatigue crack growth rate vs. the stress intensity factor range with $R = 0.5$ and $P_{O_2} = 9.44 \times 10^{-6}$ atm. ... 48
Figure 24. Fatigue crack growth rate vs. the stress intensity factor range with $R = 0.5$ and $P_{O_2} = 4.82 \times 10^{-5}$ atm. ..... 49

Figure 25. Fatigue crack growth rate vs. the stress intensity factor range with $R = 0.5$ and $P_{O_2} = 9.46 \times 10^{-4}$ atm. ..... 49

Figure 26. Fatigue crack growth rate vs. the stress intensity factor range with $R = 0.5$ and 0.1 Hz loading...................... 50

Figure 27. Fatigue crack growth rate vs. the stress intensity factor range with $R = 0.5$ and 2 Hz loading.................. 51

Figure 28. Large plot shows crack growth vs. time at $K = 49.5$ MPa/m under static loading conditions. The smaller crack growth rate vs. oxygen partial pressure plot in the upper left corner illustrates the decrease in growth rates as the oxygen concentration is increased.................................................. 52

Figure 29. Crack growth rate vs. oxygen partial pressure for static loading at $K = 33.0$ MPa/m.......................... 54

Figure 30. Scanning electron micrographs of typical fracture surface. The transition from fatigue to static loading is shown at a higher magnification in the latter micrograph and demonstrates a clear interface between transgranular and intergranular failure. ........................................................................................................... 55

Figure 31. Scanning electron micrograph of specimen oriented edge-on to show transition between fatigue and static loading. Also shown is the crack tip region................................................... 56

Figure 32. Secondary electron image taken inside the intergranular fracture regime of Figure 31 showing a clearly faceted intergranular fracture surface. .......................................................................................... 56

Figure 33. SEM image taken at 2500x showing extensive intergranular crack branching................................. 57

Figure 36. Backscatter electron image showing a crack which traversed through a heavily carbided region which are distinguishable from the matrix by their faceted structure. The light and dark carbides are molybdenum and chromium rich, respectively................................................................. 61

Figure 37. A small region taken from Figure 35 showing chromium rich carbides dispersed through the matrix and also both light and dark contrast particles on the grain boundaries ....................................................... 61

Figure 38. Secondary electron image taken in a heavily carbided region with the scanning Auger nanoprobe. The image corresponds directly to area in which compositional maps were obtained............................... 63

Figure 39. Compositional mapping results of a cracked region occupied by Cr and Mo carbides. Note that an increase in intensity of an element is marked by an increase in brightness in the above images. ............ 64

Figure 40. Secondary electron image showing the three survey analysis regions taken from the carbide region: 1) matrix adjacent to carbides 2) chromium rich carbide 3) molybdenum rich carbide............. 65

Figure 41. Image showing the three survey analysis regions taken near a crack tip in which the specimen was tested with $K = 30$ MPa/m and $P_{O_2} = 9.46 \times 10^{-4}$ atm (~1000 vppm O$_2$ in Ar). Description of each region as follows: 1) matrix far from crack 2) inside fracture surface 3) on grain boundary ahead of crack........ 66

Figure 42. Image showing the analysis line traversing a grain boundary ahead of a crack in which resulted from loading at $K = 30$ MPa/m and $P_{O_2} = 9.46 \times 10^{-4}$ atm.......................................................... 68

Figure 43. Line scan analysis results of the line shown in Figure 42 revealing an increase in chromium on the boundary and a decrease in both oxygen and nickel.............................................. 68

Figure 44. Line scan performed approximately 5 µm further on the same grain boundary as Figure 42................. 69

Figure 45. Line scan analysis results of the line shown in Figure 44 revealing an increase in chromium and carbon and a decrease in oxygen and nickel on the boundary. The dark particle the line intersects on the left side yields an increase in chromium and carbon indicating a chromium rich carbide................................. 69

Figure 46. Image showing an area ahead of a crack which fractured under loading at $K = 30$ MPa/m and $P_{O_2} = 9.46 \times 10^{-4}$ atm (~1000 vppm O$_2$ in Ar). The image corresponds directly to the area in which compositional maps were obtained......................................................... 70

Figure 47. Compositional mapping images of the grain boundary region directly ahead of a crack tip shown in Figure 46................................................................. 71
Figure 48. Micrographs of an oxidized intergranular fracture surface from a sample tested at K = 30 MPa/m and P_{O_2} = 4.82 \times 10^{-5} \text{ atm} (~50 \text{ vppm} \text{ O}_2 \text{ in Ar}). The lower magnification image on the left is the backscatter electron image showing where the line scan on the secondary electron on the right was taken.  

Figure 49. Line scan analysis results showing the nickel, molybdenum, and carbon intensities superimposed on the secondary electron image of the analysis region.  

Figure 50. Line scan analysis results showing the chromium and oxygen intensities superimposed on the secondary electron image of the analysis region.  

Figure 51. Image showing the three points used to conduct a survey analysis on and near the intergranular fracture surface. Description of each point as follows: 1) one of numerous particles which was visible in a number of SE images 2) directly adjacent to fracture surface on apparent oxide 3) matrix for baseline.  

Figure 52. Image on the left showing the region the line scan analysis was performed ahead of an intergranular crack. The high magnification image on the right shows the placement of the lines with line 1 directly ahead of the visibly oxidized surface and line 2 on the grain boundary.  

Figure 53. Line scan analysis results for line 1 overlaid on the high magnification image in Figure 52 showing the intensities of chromium, nickel, oxygen, and carbon.  

Figure 54. Line scan analysis results for line 2 in Figure 52.  

Figure 55. Six lines scans performed in the same region as Figure 52. Each line was placed so that it runs perpendicular to the grain boundary in the center of the picture.  

Figure 56. Line scan analysis results for line 1 superimposed on the image in Figure 55 showing the intensities of chromium, nickel, carbon, and oxygen.  

Figure 57. Line scan analysis results for line 2 superimposed on the image in Figure 55.  

Figure 58. Line scan analysis results for line 3 superimposed on the image in Figure 55.  

Figure 59. Line scan analysis results for line 4 superimposed on the image in Figure 55.  

Figure 60. Line scan analysis results for line 5 superimposed on the image in Figure 55.  

Figure 61. Line scan analysis results for line 6 superimposed on the image in Figure 55.  

Figure 62. Fatigue crack growth rates vs. oxygen partial pressure for R = 0.5 and 0.1 Hz loading. Note that the oxygen partial pressure range from 10^{-19} \text{ to } 10^{-7} is omitted since there is no data in this region.  

Figure 63. Fatigue crack growth rates vs. oxygen partial pressure for R = 0.5 and 2 Hz loading.  

Figure 64. Crack growth rate vs. oxygen partial pressure plot comparing static loading at K = 33.0 MPa/m and the 250s loading, 500s hold, 250s trapezoidal waveform at K_{max} = 33.0 MPa/m and R = 0.875.  

Figure 65. Intergranular oxygen penetration as a function of test temperature compiled from literature data on Ni270, Rene 80, IN718, and A286 [42].  

Figure 66. Crack growth rate vs. oxygen partial pressure under sinusoidal loading at K_{max} = 33.0 MPa/m, f = 0.01 and R = 0.625.  

Figure 67. Crack growth rate vs. oxygen partial pressure under sinusoidal loading at K_{max} = 33.0 MPa/m, f = 0.005 and R = 0.75.
LIST OF TABLES

Table 1. Nominal Chemical Composition of Inconel Alloy 617 (in wt. %) .............................................. 34
Table 2. Tensile Properties of Inconel Alloy 617 (at -25°C) ................................................................. 34
Table 3. Survey analysis results of the three regions analyzed in Figure 40. Note that the results are in percentages for each element and are not absolute values, meaning each region must sum to 100% ....................... 65
Table 4. Survey analysis results of the three regions analyzed in Figure 41 .................................................. 67
Table 5. Survey analysis results of the three points pictured in Figure 51 .................................................... 75
Table 6. Fatigue crack growth rate data with R = 0.1 and using a gas mixture of 1000 vppm O2 in argon. ....... 96
Table 7. Fatigue crack growth rate data with R =0.1 and $P_{O_2} < 2 \times 10^{-12}$ atm ........................................ 96
Table 8. Fatigue crack growth rate data with R = 0.5 and $P_{O_2} < 2 \times 10^{-21}$ atm ...................................... 97
Table 9. Fatigue crack growth rate data with R = 0.5 and using a gas mixture of 10 vppm O2 in argon. .......... 97
Table 10. Fatigue crack growth rate data with R=0.5 and using a gas mixture of 50 vppm O2 in argon. Also shown is the static loading crack growth rate data at K = 49.5 MPa/m with varying oxygen partial pressure used for Figure 28 .................................................................................................................. 98
Table 11. Fatigue crack growth rate data with R=0.5 and $P_{O_2} < 2 \times 10^{-17}$ atm ........................................ 98
Table 12. Fatigue crack growth rate data with R = 0.5 and using a gas mixture of 1000 vppm O2 in argon ........... 99
Table 13. Fatigue crack growth rate data with R=0.5 and using a gas mixture of 1000 vppm O2 in argon. Also shown is the static loading crack growth rate data at K = 33.0 MPa/m with varying oxygen partial pressure conditions ................................................................. 99
Table 14. Static loading crack growth rate data at K = 33.0 MPa/m using a gas mixture of 1000 vppm O2 in argon. Note that the fatigue steps documented in this table were necessary to promote crack growth under static loading ......................................................... 100
Table 15. Crack growth rate data at various $\Delta K$ values for fatigue loading and static at K = 33.0 MPa/m using a gas mixture of 50 vppm O2 in argon ................................................................. 100
Table 16. Crack growth rate data at various $\Delta K$ values for fatigue loading and static loading at K = 33.0 MPa/m and $P_{O_2} < 4 \times 10^{-21}$ atm .......................................................................................... 101
Table 17. Peter L. Andresen’s closed form fit DCPD equation developed from finite element analysis .......... 105
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1. INTRODUCTION

Advanced energy production systems, including high temperature gas reactor systems, will require the use of metallic materials at temperatures as high as 1000°C. The Next Generation Nuclear Plant (NGNP) is being developed to produce heat for hydrogen production as well as electricity without emission of greenhouse gases. This will require the outlet temperature of the reactor to approach 950°C. In the NGNP, the intermediate heat exchanger will perform the critical function of transferring heat from the primary reactor helium to a secondary working fluid at a slightly lower temperature. The combination of very high operating temperature, temperature gradients and pressure (7-8 MPa) could produce large stresses at metallic joints/welds. Current candidate materials are limited to solid-solution strengthened alloys containing chromium which have high creep resistance and stable environmental resistance properties due to the high chromium content. Proposed alloys for service include Ni-Fe-Cr based alloys such as Alloy 800, and Ni-base superalloys such as Alloy 617 and Alloy 230. Several of these alloys have been approved for non-nuclear construction in Section VIII of the ASME boiler and pressure vessel design code but only Alloy 800 is allowed under the nuclear construction requirements in Section III. Section III allows Alloy 800 operation of up to approximately 750°C. A draft code case for Alloy 617 was submitted in the late 1980s, but it was concluded that there was insufficient information on creep-fatigue behavior and high temperature weldment fatigue data to allow code qualification. Much of the current work to expand the knowledge base of the synergistic effects of environment, loading, and temperature is being performed on Alloy 617 since it appears closest to gaining code approval, but other alloys such as Haynes Alloy 230 are still backup candidates and part of current research programs.

In the temperature range of 0.3-0.6 T\(_m\) (and sometimes up to 0.75 T\(_m\)) where creep relaxation of stresses at crack tips is not significant, the initiation and propagation of fatigue or stress corrosion cracks needs to be taken into serious consideration and could greatly complicate analysis of expected behavior and life prediction of these materials should cracks initiate during operation. For the case of high temperature gas reactor systems, the environment consists of very pure helium but will nonetheless contain small amounts of gaseous impurities, including H\(_2\), CO, CH\(_4\), H\(_2\)O, and CO\(_2\). Depending on the concentration of these species the chemical potential can be either slightly oxidizing or reducing (carburizing). The above alloys, while exhibiting
superior creep and tensile properties, were designed to operate in a highly oxidizing environment where the formation of protective chromia (or alumina) based films predominate. At very low oxygen potentials, where the protective film may not be stable, these materials are not optimized and may be susceptible to embrittlement by oxygen transport along grain boundaries and the effects of decarburization. Oxygen may diffuse or be transported down the grain boundaries in this potential range and embrittle the material in the presence of an applied stress. This effect usually manifests itself as a change in crack path from transgranular to intergranular and an increasing crack growth rate with decreasing oxygen concentration over a specific oxygen concentration range.

Early work by Smith et al. established that low cycle fatigue life decreased with increasing oxygen partial pressure in the intermediate temperature range [1]. The effect of oxygen on low cycle fatigue and stress rupture lives was later expanded to superalloys, including A286, Udimet 500, and IN903A, by McMahon, Woodford, and Coffin et al. [2-7]. Having established the detrimental effects of high temperature exposure to environments with high oxygen potentials, studies of the embrittlement/oxide formation processes in various grades of nickel were conducted. These investigations mainly involved high temperature air or vacuum pre-exposure of specimens in the absence of stress (i.e. static embrittlement). High temperature tensile tests were subsequently carried out and again demonstrated that tensile ductility was most affected at intermediate temperatures for air exposed specimens [8-10]. McMahon and Coffin proposed that local oxide formation at grain boundaries preceded crack growth [2]. The mechanism they proposed began with migration of oxygen along grain boundaries under an applied stress, subsequent intergranular oxidation, and finally crack propagation due to fracture of a brittle intergranular oxide. The process then repeats itself resulting in intergranular crack growth. This mechanism was later coined “stress accelerated grain boundary oxidation” (SAGBO) by Smith et al. [11]. Another mechanism was proposed by Bricknell and Woodford who assumed that oxygen first embrittled the grain boundary and fresh fracture surfaces created by crack propagation were subsequently oxidized [5]. They observed that grain boundaries were embrittled far ahead of any visible oxidation and attributed this to long-range oxygen migration down rapid diffusion paths such as slip planes and grain boundaries. The boundary is then embrittled by the formation of brittle phases and/or solute segregation which would inhibit grain
boundary sliding/migration and the relief of local stresses during deformation. After the embrittled boundary fails in tension, the fracture surfaces are oxidized and the process repeats.

The effect of oxygen partial pressure on crack growth rates of Alloy 718, which has been used extensively in gas turbine components and more recently in structural coolant components in pressurized water reactors, has also been extensively studied [12-16]. As discussed by Molins et al., Alloy 718 exhibits a sharp transition in crack growth rates at an oxygen partial pressure between approximately $10^{-4}$ and $10^{-3}$ torr [13]. The transition is independent of the stress intensity factor, and the crack propagation mode changes from transgranular below the critical partial pressure to intergranular at pressures above this value. Other alloys have also demonstrated this same stepped phenomenon [17, 18]. The sharp crack growth transition can be attributed to the oxygen partial pressure for oxide formation. In TEM analysis of the fatigue samples studied by Molins et al., an outer scale was identified as a nickel-base, iron-rich oxide which was the first oxide to appear [14]. Later, a protective fine grain subscale was formed which was identified as Cr$_2$O$_3$. The embrittlement was concluded to result from the porous nickel-base oxide formation during the early stage of oxidation which allowed oxygen ingress along grain boundaries before the protective chromium oxide film could form. At lower oxygen partial pressures or for high chromium contents, preferential chromium oxidation occurs and the environmental damage is minimal [19, 20]. Other recent work has demonstrated that Alloy 718 is susceptible to a phenomenon called dynamic embrittlement [21, 22]. This differs from static embrittlement in that it involves surface absorption of an embrittling element into grain boundaries under an applied stress which leads to time dependent intergranular fracture. The features of this type of fracture were first studied in the oxygen-induced cracking of Ni$_3$Al [23] and sulfur-induced cracking of low-alloy steels [24]. The term “dynamic embrittlement” was coined [23, 25] since the embrittlement process occurred during the application of stress rather than in the unstressed condition.

While these intergranular crack growth phenomena, which can be categorized as subsets of stress corrosion cracking, have been well documented for many alloy systems, the effect of low concentrations of oxygen on crack growth in nickel superalloys proposed for the Next Generation Nuclear Plant (NGNP) is largely absent, including Alloy 617. For this reason, it is critical that the effect of the gas reactor environment on these materials be fully explored. The development effort has thus largely focused on obtaining properties at the maximum expected

13
operating temperatures. In this temperature range, creep and creep-fatigue interactions are expected to be dominant. However, the full operating temperature range will cover the range 450-950°C. At the lower end of this temperature range, cracks may initiate (or be present in the as-fabricated condition) and propagate due to either fatigue or static loading where a substantial stress can be maintained at crack tips. Additionally, at the very low oxygen potentials which will exist in the NGNP it may be possible for the oxygen partial pressure to fall below the NiO equilibrium and even approach the Cr₂O₃ equilibrium pressure. If the protective oxide layer becomes unstable, then oxygen induced embrittlement will be a possibility despite the high chromium content in Alloy 617 (~22 wt%) meant to provide environmental resistance [14, 20].

In this study, the crack growth behavior of Alloy 617 is explored in the stress intensity factor and low oxygen potential range expected to exist in the NGNP heat exchanger systems. In particular, the effect of oxygen potential on constant K (static loading) and constant ΔK (fatigue loading) crack growth has been tested. Furthermore, various frequencies and stress intensity factors were explored at each oxygen partial pressure. Finally, detailed analysis of intergranular fracture surfaces and crack tips was conducted using high resolution SEM and Auger spectroscopy analysis.
2. BACKGROUND

The literature reviewed in this section will mainly focus on time dependent cracking in nickel-base alloys and the environmental interaction of oxygen at the crack tip. However, there is a much broader range of literature which encompasses the crack growth mechanisms relevant to this research. These related crack growth processes/mechanisms will be briefly discussed to help understand and characterize both bulk and crack tip damage mechanisms. Furthermore, a discussion of a broad range of topics will facilitate in making impartial conclusions about proposed mechanisms based on the results presented in this work.

2.1 Time Dependent Fatigue Crack Growth

The research on elevated temperature fatigue life of engineering alloys as a function of oxygen partial pressure began in the sixties. Some of these early works focused on nickel and stainless steel and showed that the fatigue life decreased as the oxygen partial pressure increased [1, 26]. Furthermore, at intermediate temperatures, there appeared to be a sharp transition in low cycle fatigue life at a critical oxygen potential in some cases. The study of environmental effects on low cycle fatigue life was extended to superalloys mainly by McMahon, Woodford, and Coffin et al. [2-4]. High vacuum equipment was used to compare crack growth rates in both air and vacuum at high temperatures. Room temperature tests were also conducted as a baseline for the experiments. The conclusion found in all of the studies was that low cycle fatigue lives in air were significantly less than those in vacuum at high temperatures, sometimes by approximately an order of magnitude, for a variety of alloys including A286, stainless steel, and Udimet 500. Upon analysis of the fracture surfaces, the material had failed via transgranular propagation in all vacuum tests, while the high temperature air tests showed intergranular or mixed mode crack propagation.

In the early testing of superalloys under varying environmental conditions, a significant temperature effect was also observed in low cycle fatigue experiments. Namely, there was an intermediate temperature at which the fatigue life was a minimum. Figure 1 plots the fatigue life of IN706 as a function of temperature from approximately room temperature conditions to 800°C for both vacuum and air [4]. At ~700°C, there was a pronounced minimum in fatigue life in the
air tests. The authors of the work also noticed a slight minimum for the vacuum tests at the same temperature but concluded this was possibly a result of failing to accomplish completely inert conditions in their experimental setup or damage resulting from an independent creep component. This data again confirmed that environmental contributions can lead to a reduction in fatigue life at elevated temperatures.

Since fatigue life investigations were revealing a transition from transgranular to intergranular cracking, more work was completed to study the critical frequencies, oxygen potentials, and temperatures at which this transition to time dependent growth occurred. It should be noted that fatigue crack growth is time dependent if the growth rate increases with increasing temperature and/or decreasing frequency. Sadananda et al. reviewed the effects of many test variables, including frequency, hold time, temperature, load, and environment, on crack growth in a variety of nickel-base superalloys [27-29] and found that time dependent crack growth was sensitive to oxygen potential, temperature, and microstructure. The tests conducted at higher fatigue frequencies in the cycle dependent regime showed little to no changes when

![Figure 1. Fatigue life of IN706 as a function of temperature under air and vacuum conditions [4].](image-url)
these factors were varied. The time dependent regime was where intergranular cracking was found to occur. Furthermore, the work demonstrated that time dependent crack growth was significantly sensitive to microstructural changes. A clear illustration of the transition from time dependent to time independent crack growth was given by Pédrón et al. from the fatigue crack growth rates in Alloy 718 [30] as shown in Figure 2. The increase in crack growth rates with decreasing frequency indicates a time dependent process, which the authors attributed to enhanced growth rates due to environmental attack. The reason that time dependency becomes more prevalent at lower frequencies was concluded to be a result of oxidation effects [31]. In addition, time dependent crack propagation is a thermally activated time dependent processes and thus become more severe with increasing temperature [32]. More recent papers discussed in depth the oxidation and grain boundary diffusion kinetics in Alloy 718 as a function of hold time and stress intensity factor [15, 33, 34] and again found that high temperature crack growth is a fully environmental time dependent process.

Around the time research was distinguishing between time dependent and independent fatigue, much of the early work assumed that an independent creep component was responsible for the time dependence. However, the work completed by Coffin, Woodford, and others demonstrated the major contribution of the environment to time dependent fracture [2-4, 32].

![Figure 2. Change in fatigue crack growth rate with test frequency and temperature for Alloy 718 at ΔK = 40 MPa√m [30].](image-url)
The term presently used to describe this phenomenon is creep fatigue environment interaction. Similar to calculations for time independent crack propagation based on linear elastic fracture mechanics below creep loads, time dependent cracking of nickel-base alloys relate to the stress intensity factor for specific conditions (i.e. temperature, environment, cycle frequency). A considerable amount of work has been conducted on Inconel alloy 718 over a range of temperatures and environmental conditions [15, 27-31, 35, 36].

As seen in much of the discussion so far, it is widely believed that the enhanced crack growth rates at elevated temperatures is due mainly to the environment, namely the oxygen in tests conducted in air. This statement has been validated by conducting fatigue tests at a constant ΔK value under varying oxygen partial pressure conditions. The results from Molins et al. clearly demonstrated a critical oxygen partial pressure at which the crack growth rate changes significantly [13, 18, 37]. These results are shown in Figure 3 which plots da/dN vs. oxygen partial pressure for two different stress intensity factor ranges. A sharp increase in the crack growth rates by approximately two to three orders of magnitude was observed between 10^-4 and 10^-3 torr. In this transition region, the increase in crack growth rate was concluded to be a result of delayed passive oxide formation [14]. At the extremes of the oxygen partial pressure range, the growth rates were nearly constant. The saturation of the crack growth rates above 10^-3 torr was attributed to the buildup of a protective chromium oxide film at the crack tip.

![Figure 3. Constant ΔK fatigue crack growth rates as a function of oxygen partial pressure in Alloy 718 [37].](image-url)
2.2 Static Embrittlement

The term static embrittlement refers to the process of environmentally induced embrittlement which occurs during exposure at high temperature in an unstressed condition. This should be distinguished from dynamic embrittlement, the environmentally sensitive fracture process which occurs during sustained specimen loading and manifests itself as a discontinuous intergranular crack growth process. Dynamic embrittlement and its features will be discussed in the following section.

2.2.1 Effect of environment

Much of the work studying the process of oxygen diffusion and embrittlement was done in the seventies and eighties, especially on various grades of nickel [8-10]. It was also shown that many nickel, iron, and cobalt superalloys were susceptible to oxygen damage [5-7]. In general, the penetration and damage depth increased with increasing time and temperature, but the tensile ductility and creep life were a minimum at intermediate temperatures. This is similar to the minimum found for LCF lives in nickel-base superalloys as shown in Figure 1. Another common aspect between these early investigations was the recognition of a strong sensitivity to composition, especially in varying chromium content. It was found that increasing the chromium concentration, using protective coatings, or doping with boron could actually prevent penetration of oxygen or slow down the kinetics of oxygen diffusion along grain boundaries [8, 10, 38]. The early work conducted by Bricknell and Woodford on various grades of nickel helped build the framework to understand the common damage mechanisms found in various alloy systems, as well as the embrittlement processes which occur ahead of propagating cracks.

Bricknell and Woodford reported on the embrittlement of nickel following high temperature exposure in air and vacuum and recognized that the damage process was intrinsic to both pure nickel and nickel-base superalloys [10]. Figure 4 shows their results on Ni270 following 1000°C air and vacuum exposure prior to testing at various temperatures in vacuum. The tensile ductility of the samples was represented by the percent reduction in area during high temperature tensile tests. At intermediate temperatures (700 ~ 800°C), there was a drastic loss in ductility following air exposure. Furthermore, there was slight minimum in ductility following vacuum exposure, which apparently was removed for specimens machined from the center of a large block.
Figure 4. The effect of 200 hr of air and vacuum exposure at 1000°C on the tensile ductility of Ni270 at a variety of temperatures [10]. The two open circles are samples machined from the centers of blanks after vacuum exposure.

following vacuum exposure. At higher temperatures, some of the ductility was restored which may be similar to the reported fatigue lives in Figure 1. Various environmental atmospheres including oxygen, nitrogen, carbon dioxide, carbon monoxide, and a Ni/NiO pack were also used in the exposure at 1000°C prior to tensile testing. It was determined that oxygen was the embrittling species since the % R.A. was approximately between 90 to 100% for the environments containing no oxygen. The Ni/NiO pack produced an oxygen partial pressure of < 10^{-7} torr which allowed for some oxygen embrittlement to occur. Similar experiments were conducted a less pure grade of nickel, Ni200. Oxygen embrittlement is acutely shown in the SEM micrographs of the fractured Ni200 tensile specimen shown in Figure 5. The vacuum annealed specimen in Figure 5a demonstrated complete ductile rupture and necked down to a point, whereas as the air exposed specimen in Figure 5b showed intergranular fracture. To test whether embrittlement extended past the internal oxidation zone visible to approximately 250 μm from the outer circumference in Figure 5b, a sample was tested where more than twice the thickness of the internally oxidized zone was machined. The fracture was again intergranular with a 13% reduction of area upon failure. The authors concluded that intergranular embrittlement penetrated far in advance of matrix internal oxidation.
The embrittlement results on pure nickel should be compared to the findings in the research on the nickel-base superalloy Udiment 500 [2]. Even though the Udiment 500 specimens were tested in low cycle fatigue, the author considers this to be the appropriate section to compare the crack propagation process originally proposed by McMahon and Coffin on their Udiment 500 work to that of Bricknell and Woodford. The mechanism proposed by McMahon and Coffin starts with intergranular oxidation which was assumed to occur on boundaries where high stress concentrations existed. The oxide was presumed to crack in tension under stress, allowing new oxide to form at the crack tip and the process to repeat. This process is in contrast to that proposed by Bricknell and Woodford in their static embrittlement experiments on iron-base superalloy IN903A. From their findings, they suggested that the boundary is first embrittled by intergranular oxygen diffusion which causes the boundary to fail in tension. The boundaries which have been directly exposed to the oxidizing environment are oxidized only after fracture. The process repeats itself as oxygen is able to diffuse further down the grain boundary and the next segment of the embrittled grain boundary fractures ahead of the crack tip. There is unequivocal agreement that the oxygen in the environment is the damaging species but the question still remains whether the enhanced crack growth rates are due to intergranular oxidation or embrittlement. Current work is determining the nature of grain boundaries ahead of propagating cracks and more information is revealed as new analysis methods such Auger nanoprobe spectroscopy and atom-probe tomography are used.
2.2.2 Role of microstructure

In contrast to the evident oxygen sensitivity of pure nickel and some superalloys, there have been reports of some alloys and special treatments of the metals which can mitigate or almost completely eliminate oxygen embrittlement. High chromium alloys such as Hastelloy X (22 wt. % Cr) show no sensitivity to prior high temperature exposure in air as indicated by results in Figure 6. The stable chromium oxide scale which forms on the surface of this alloy prevents further oxygen penetration, which was found to also occur in the binary Ni-Cr system [19]. The critical minimum chromium content to ensure the formation of a protective surface chromium oxide layer in the binary system is about 20 – 25 wt. % Cr [20]. In addition to adjusting chromium content, additions of boron and hafnium have been shown to be beneficial in nickel and various alloys. In the tests measuring the tensile ductility of nickel, specimens doped with boron showed no intergranular oxides beyond the region of matrix internal oxidation [6]. It was suggested that boron could block the diffusion of oxygen along grain boundaries by occupying grain boundary sites [5, 6]. Similar work was conducted on Alloy 718 and showed that doping with boron helped prevent brittle intergranular fracture [38]. Hafnium is similar to boron in that it is also a grain boundary segregant and hinders fast diffusion of oxygen along boundaries. An added benefit of hafnium, however, is that it also serves as a sulphur getter. Note that sulphur has been found to cause nickel embrittlement in the elemental form and cause more severe damage than oxygen [39].

![Figure 6. The tensile ductility of Hastelloy X as a function of temperature for specimen air exposed (open circles) and vacuum exposed (closed circles) at 1000°C before testing in vacuum [9].](image-url)
2.2.3 Possible mechanisms for oxygen embrittlement

Since oxygen embrittlement along grain boundaries was well established by the early eighties, work began to focus on the responsible mechanism. It was first recognized that oxygen did not appear to embrittlement in the elemental form (in contrast to sulfur) in pure nickel. This conclusion was based on the tensile results on high purity nickel which had been decarburized prior to testing in air and showed very little embrittlement [40]. Therefore, an oxidation reaction was necessary for embrittlement and impurities such as carbides were suspected to be involved in the reaction. Examples of these reactions were found in a variety of cases. Vacancies which appeared on grain boundaries, previously thought to be a consequence of vacancy injection from growing oxides or creep induced cavities, were actually proven to result from carbon monoxide and dioxide gas bubble formation [41]. Chemical reactions involving the oxidation of sulphides on grain boundaries leading to sulphur embrittlement were also found to occur [39]. Finally, high grades of nickel, which were initially free of intergranular carbides and sulphides, showed formation of complex oxides from trace impurities along grain boundaries [8].

In a recent review paper by Woodford, the author concisely summarizes the four processes which appear to be akin to intergranular oxygen embrittlement: gas bubble formation (CO and CO₂), release of sulphur upon oxidation of sulphides, precipitation of oxides, and solute segregation [42]. Furthermore, it was pointed out that oxygen causes a chemical reaction (possibly with carbon) which affects the process of grain boundary separation and results in intergranular fracture as opposed to decohesion of grain boundaries caused by sulphur embrittlement. The mechanism by which intergranular oxidation could affect ductility in nickel was first proposed by Bricknell and Woodford. Their observations indicated that dynamic recrystallization did not occur in specimens exposed to air at 800°C prior to testing while the vacuum exposed specimens did show signs of recrystallization. Thus, a link between grain boundary mobility and embrittlement (in oxygen containing environments) was established as was previously reported for both copper and silver under similar conditions. The transition between grain boundary sliding and pinning is shown schematically in Figure 7. At low temperatures there is little or grain boundary sliding and deformation is mainly carried by slip, so ductility differences between air and vacuum exposed material is minimal. At intermediate temperatures more of the deformation is carried by grain boundary sliding with slip accommodation in the near boundary regions. However, embrittled boundaries hinder grain
boundary migration and thus cracks initiate at regions of high stress concentrations when further accommodation is prevented, accordingly leading to a reduction in ductility. At high temperatures, the grain boundaries have enough thermal energy to overcome the source of pinning and ductility is restored.

2.2.4 Differences between static embrittlement and other mechanisms

During creep tests of the first low thermal expansion Ni-Fe-Co based superalloy, IN903, the term stress accelerated grain boundary oxidation (SAGBO) was established to describe the intergranular cracking found to initiate at the surface. This term has unfortunately been used far outside its scope when describing elevated temperature failure of alloys in oxygen containing environments. Figure 8 schematically illustrates the differences between SAGBO and oxygen embrittlement. As described before in McMahon and Coffin’s work on Udimet 500 [2], SAGBO involves preferential intergranular oxidation and successive cracking of that oxide. On the contrary, in the oxygen embrittlement process the grain boundary is embrittled ahead of a crack tip and oxidation occurs only when fresh fracture surfaces are exposed to the oxidizing environment. The embrittlement can occur far in advance of any oxide scale and will accelerate fracture rates depending on the oxygen partial pressure. This process is a specific example of gas phase embrittlement (GPE) and is clearly favored over the SAGBO mechanism as the source of enhanced crack growth. Even recent work on high temperature rupture behavior of IN718 and
IN909 has concluded that SAGBO is not a feasible mechanism to explain the accelerated intergranular fracture rates found in moist air [43].

### 2.3 Dynamic Embrittlement

The phenomenon of dynamic embrittlement involves surface absorption of an embrittling element into grain boundaries under an applied stress. This leads to time dependent fracture along the embrittled grain boundaries. The features of this type of fracture were first studied in the sulfur-induced cracking of low-alloy steels [24], tin-induced cracking of a Cu-Sn alloy [44], and oxygen-induced cracking of both a Cu-Be alloy [45] and of Ni$_3$Al [23]. In these studies, the term “dynamic embrittlement” was coined [23, 25] since the embrittlement process occurred during the application of stress rather than in the unstressed condition.

A recent study has shown that this kind of cracking in Alloy 718 occurs under static loading as well [21, 22]. It was already known that Alloy 718 was extremely susceptible to intergranular cracking in oxygen containing environments during hold times under stress or low frequency fatigue tests [12-16]. By testing notched bars of Alloy 718 in pure bending at high temperatures, Pfaendtner and McMahon found that the dependence of cracking on oxygen potential and the morphology of the fracture surface was essentially the same as that found in the earlier fatigue and hold time tests [22]. Furthermore, the cracking could be arrested and resumed very quickly by simply removing and readmitting the oxygen as shown in Figure 9. Thus, it was concluded
that intergranular fracture occurs if the stress concentration ahead of the crack is high enough to allow atoms to enter and diffuse along the grain boundary and cause subsequent decohesion.

The crack growth process by dynamic embrittlement in polycrystalline materials has been found to be intermittent [22]. This results from the constraint imposed on the crack tip by regions of uncracked material along the crack front which had not yet fractured. Since the rate of decohesion depends upon the rate of oxygen ingress at the crack tip along the grain boundary, the rate of cracking varies with local grain boundary structure and can thus result in intermittent cracking. Furthermore, the damage at the crack tip due to inward oxygen diffusion in the dynamic embrittlement process only requires short range diffusion (one to two nanometers) as opposed to the long range diffusion of oxygen observed in the static embrittlement studies on pure nickel [46]. As an example, a recent paper on IN738 proposed that intergranular oxygen diffusion occurs far in advance of a crack tip during a tensile hold time period. This was concluded from the result that after a hold time of 100s at 650°C and subsequent fatigue loading, a region of intergranular fracture approximately 200 to 300 μm in length was found before transgranular fracture was observed. However, this would have required a diffusion coefficient for oxygen at 650°C on the order of $10^{-6}$ cm$^2$/s which is much too high. For reference, oxygen diffusivity in Ni270 (by extrapolating data to 650°C) was predicted to be approximately

![Figure 9. Load relaxation curve resulting from cracking of Alloy 718 in oxygen at 650°C loaded in pure bending at fixed displacement. Note that crack growth was completely arrested when the test chamber was evacuated to below ~$10^{-2}$ Pa [22].](image-url)
10^{-15} \text{ m}^2/\text{s} in one paper [47]. The features of the dynamic embrittlement mechanism better supports the results of the IN738 study.

Building upon the observation that crack growth rates can vary with grain boundary structure, a study of dynamic embrittlement was conducted on symmetric tilt boundaries of \( \Sigma 5 \) in bicrystals of a Cu-Sn alloy [48]. It was found that cracking occurred continuously in the direction of the tilt axis which is expected in a bicrystal free from the constraints found in a polycrystalline material. Additionally, cracking did not occur in the slow-diffusion direction normal to the tilt axis demonstrating the effect of diffusion rate on crack growth rates. Given the dependence of fracture rates on grain boundary orientation, the effect of grain boundary engineering type processing to produce a higher percentage of special coincident site lattice (CSL) grain boundaries in a given material became increasingly appealing. Bending and oxidation experiments were conducted on IN718 specimens that underwent successive steps of deformation and annealing to increase the fraction of CSL boundaries [49, 50]. The greatest increase in the percentage of special CSL grain boundaries was with the \( \Sigma 5 \) boundaries, producing an increase from 16.5% in the as-received conditioned to 34% after four thermomechanical processing cycles. The load relaxation curve results from the experiments shown in Figure 10 clearly show that the grain boundary engineered alloy had a higher resistance to both intercrystalline oxidation and hold time cracking via dynamic embrittlement. Thus, it has been shown that grain boundary engineering type processing has considerable benefits in engineering alloys including nickel-base superalloys.

2.4 Crack Tip Embrittlement and Oxidation

In the previous sections, the commonalities between various types of high temperature time dependent crack growth have been established. The relations to both static and dynamic embrittlement have also been discussed. In general, there is a critical oxygen potential below which no time dependent cracking and/or embrittlement takes places. The dominant process in all types of embrittlement involves intergranular oxygen transport which, unlike sulfur, does not appear to embrittle in the elemental form and requires an oxidation reaction on the grain boundary for embrittlement to occur. Common reactions involve oxidation of impurities or minor alloying elements, and gas bubbles formation resulting from oxidation of carbon and
Figure 10. Effect of grain boundary engineering (via thermomechanical processing) on the fixed displacement load-relaxation curves for Alloy 718 at 650°C in air.

 carbides which can reduce the ability to relieve stress concentrations during grain boundary sliding. Gas bubble formation can also lead to creep cavity nuclei and cause direct intergranular fracture, although this process is less common [51]. The fact that oxidation reactions are necessary for intergranular embrittlement was confirmed by the resistance of decarburized high purity nickel to oxygen embrittlement [40]. The theory of time dependent cracking by intergranular diffusion of oxygen and oxidation reactions is challenged by the idea of the successive cracking of an intergranular oxide (i.e. SAGBO) [11]. However, formation of an oxide is not a necessary requirement to trigger increases in crack growth rates when oxygen concentrations are increased in the environment. Another postulation was that a shift in rate control from diffusion into the crack tip region (i.e. ample supply of gaseous embrittling element) to delivery of the gaseous embrittling agent to the crack tip (i.e. lower range of partial pressures) would cause time dependent cracking. Yet, this conclusion was reached even though normal diffusion processes and oxidation at the crack tip were observed [22].

2.4.1 Microstructural crack tip observations in IN718 and similar alloys

Even though there have been many extensive studies on fracture, creep, and embrittlement/oxidation in many major engineering alloys in a variety of environments, there is
still much to be understood about the nature of local interactions at the crack tip. Since the depth of oxygen penetration is so small (approx. 50 nm in some cases) in the relevant intermediate temperature regime (approx. 500-650°C), studying the interaction of oxygen at a propagating crack tip and ahead poses a considerable challenge. Many of the current theories around crack tip oxygen interactions have been drawn from static embrittlement investigations in which much greater penetration depths were involved. Nonetheless, some studies have attempted to characterize the region ahead of crack tips resulting from fatigue and sustained loads. In a microanalysis study of IN718, regions ahead of crack tips, resulting from creep crack growth experiments [16], showed strong segregation of niobium on grain boundaries [52]. The authors suggested that formation and subsequent fracture of a brittle niobium oxide film on the boundary surfaces deteriorated the crack growth resistance of the alloy since the environmental sensitivity of the alloy to oxygen increased with the niobium concentration. Further studies indicated an absence of environmental sensitivity in a Nb-free, Ni-Cr-Fe ternary alloy and supported the postulation that niobium has a significant role in the enhancement of crack growth in oxidizing environments [53]. However, later results in a niobium-free alloy showed that cracking was still significantly enhanced by oxygen in the environments and the effect of niobium content on environmental sensitivity was unclear [54].

Various investigations have been conducted ahead of crack tips formed in nickel-base superalloys using high resolution SEM, TEM, and Auger spectroscopy. Andrieu and Molins et al. proposed that oxidation in IN718 occurs in two stages starting with spinel oxide formation and subsequently chromium oxide formation at the oxide-metal interface as shown in Figure 11 [14]. In their TEM studies, the inner layer at the metal-oxide interface was identified as Cr₂O₃ while the outer layer was identified as a spinel oxide Ni(FeCr)₂O₄ in the same order as suggested in the proposed model. The conclusion reached from the data was that delay in forming the passive chromium oxide allowed deeper oxygen ingress and increase in crack growth rates. Similar reports have attempted to characterize the crack tip oxides which formed in IN718 and IN706 after fatigue crack propagation tests [55]. The findings indicated that complex oxides of Ni-Fe and Cr-Nb formed on the fracture surfaces, sometimes showing the dual-layer oxide structure. These observations, however, could not be connected to the crack growth rate data nor the TEM microstructural observations on grain boundaries ahead of crack tips by a mechanism such as intergranular oxidation or cavitation.
2.4.2 Related high temperature corrosion and oxidations studies

To widen the scope of discussion, it is useful to include a brief review of related studies that do not necessarily fall under the category of crack tip embrittlement/oxidation investigations but are nonetheless relevant. This is due to the lack of material available specifically in crack tip microstructure investigations and data in more recently developed alloys such as Inconel 617 and Haynes 230. These related studies include experiments in which the embrittling agent was not delivered by a gas but instead super critical water (SCW) and high temperature corrosion tests conducted on unstressed materials.

Since the focus of work in this thesis is on Inconel Alloy 617, some consideration will be given to the available research on corrosion in this alloy. One study investigated the corrosion effects of exposure of this alloy to helium atmospheres containing small amounts of impurities (H₂, H₂O, CO, CO₂ and CH₄) [56]. The work demonstrated that below a critical temperature of about 825°C, the presence of CO can cause simultaneous oxidation (producing Cr₂O₃) and carburization. Furthermore, reaction products resulting from exposure to He-H₂-H₂O were
analyzed using various analytical methods (SEM, Auger spectroscopy, SIMS, etc.) and found that a dense Cr₂O₃ layer formed on the surface with a sublayer of internal oxidation characterized by lenticular Al₂O₃ particles. Another study on Alloy 617 studied the effect of the grain boundary engineering treatments (via therrmechanical processing) on the corrosion resistance and mechanical properties using supercritical water exposure tests and then analyzed oxide formation using various microstructural analysis methods [57]. It was clear from x-ray diffraction data that oxide scales formed on both the as-received and the thermomechanically processed samples which were composed of chromium oxide and a spinel such as (Ni,Co)Cr₂O₄. The authors also deduced that the oxide scale on the thermomechanically processed material exhibited a higher fraction of chromium oxide than that on the as-received (unprocessed) material. Further analysis was conducted using XPS and showed that nickel and cobalt were present on the unprocessed material surfaces. This finding substantiated the x-ray diffraction data and the conclusion that oxide scale on the as-received sample is either composed of a discontinuous chromium oxide or complex oxides. In contrast, the thermomechanically processed material surface was concluded to be covered by a continuous chromium oxide since the grain boundary engineering allowed more uniform diffusion of oxygen.

Expanding on the discussion of oxide formation in supercritical water, there have been many more studies focused on the characterization of intergranular corrosion in Alloy 600. The susceptibility of nickel-base Alloy 600 to intergranular stress corrosion cracking (IGSCC) in high temperature water at low electrochemical potentials has been recognized for almost 50 years. Today, cracking of Alloy 600 components and its weld metals in the primary coolant circuits of pressurized water reactors (PWRs) has become a serious issue for life extension and thus a topic of high interest. U-Bend samples of Alloy 600 tested in 330°C pressurized water reactor water were characterized by analytical transmission electron microscopy [58]. Although analysis ahead of primary crack tips was difficult due to high local plastic deformation, predominantly nickel oxide was found on crack walls and immediately ahead of secondary crack tips. Grain boundaries, which intersected the open crack and were thus attacked by the high temperature primary water up to several microns, showed similar NiO oxides with local areas of chromium and nickel rich metal along most of the degraded zone. However, at the ends of the intergranular attack, the structure was identified as a porous Cr₂O₃ which extended about 10-50 nm. The authors suggested these results indicate a local dissolution or oxidation process and
formation of a porous structure at grain boundaries as the mechanism for IGSCC. Similar work confirmed these results and additionally proposed that the porous chromia and nanocrystalline NiO can provide a path for intergranular oxygen diffusion and cause IGSCC initiation [59]. Type 304 stainless steel is also used widely in PWRs and very recent work on these alloys has demonstrated the ability to map the oxide chemistry in intergranular cracks by NanoSIMS [60]. The study found indications of a dual oxide layer consisting of an inner chromium rich oxide layer and an outer iron rich oxide layer on the crack flanks, which agreed with a previous work by Terachi et al. on type 316 stainless steel [61]. Furthermore, oxide penetration along crystallographic deformation bands into grains adjacent to the crack was observed which had never been reported in the literature before. As NanoSIMS is able to provide high spatial resolution along with detailed compositional data of oxides and even ppm sensitivity of minor segregants, more interest is being given to analysis of stress corrosion cracks with this tool.

In summary, the research discussed in this section covers a wide range of alloys and intergranular fracture resulting from various environmental conditions. Similar crack growth and oxidation processes may be present in other nickel-base alloys in which there is more limited data, such as Alloy 617. Although the Auger spectroscopy analysis of crack tips conducted in this work does not provide the resolution of analytical TEM methods nor the mass resolution of NanoSIMS, the author hopes to connect aspects of the review here to results from the microstructural analysis of Alloy 617.
3. EXPERIMENTAL PROCEDURES

The effect of varying oxygen potential on crack growth in Alloy 617 under both static and fatigue loading conditions was studied. The tests were conducted under environmental and mechanical loading conditions which are comparable to conditions predicted for components made of the alloy. The temperature was held constant at 650 ± 3°C for all tests, and the oxygen partial pressure was varied in the test chamber by circulating either ultra-high purity argon gas or commercially pre-analyzed gaseous mixtures of oxygen and argon from 10 to 1000 vppm oxygen in argon. In all cases, the oxygen potential was measured immediately adjacent to the test sample via the use of a Yitria stabilized zirconia oxygen probe. Crack growth rates were investigated using compact tension specimen with constant ΔK and K loading. A computer program was utilized to measure crack length using a direct current potential drop (DCPD) technique. The program also communicated with the load frame controller so that crack growth rates could be obtained under constant ΔK conditions.

The precise control of test conditions such as oxygen partial pressure, temperature, and stress intensity factor (ΔK or K for fatigue and static loading, respectively) allowed easy distinction between fracture surface features resulting from varying mechanical and loading conditions. Post mortem analysis included SEM imaging to examine transgranular and intergranular cracking features. Some specimens, in which the only variable was oxygen partial pressure during crack growth, were also examined with Auger Electron Spectroscopy (AES). This analysis technique allowed for much higher sensitivity of elemental composition variations in the crack tip region so that diffusion and/or segregation of oxygen and solute atoms could be detected.

3.1 Materials

The Alloy 617 material used in this study was obtained through Special Metals, Inc. (Huntington, West Virginia). Fabrication of the alloy involved a double melting process: vacuum induction melting and electroslag remelting. The supplied plate (heat XX2834UK) was formed by cold rolling down to a thickness of approximately 19 mm (0.75 in), and subsequently
solution annealed at 1175°C. The nominal chemical composition and mechanical properties of this heat of the alloy are given in Table 1 and Table 2 respectively.

Table 1. Nominal Chemical Composition of Inconel Alloy 617 (in wt. %)

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Fe</th>
<th>Cr</th>
<th>Al</th>
<th>Ti</th>
<th>Co</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Cu</th>
<th>S</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt. %</td>
<td>3.55</td>
<td>1.69</td>
<td>21.91</td>
<td>0.96</td>
<td>0.34</td>
<td>11.42</td>
<td>0.08</td>
<td>0.11</td>
<td>0.12</td>
<td>0.04</td>
<td>0.001</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Table 2. Tensile Properties of Inconel Alloy 617 (at ~25°C)

<table>
<thead>
<tr>
<th></th>
<th>YS</th>
<th>UTS</th>
<th>% Elongation</th>
<th>% RA</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPa</td>
<td>356</td>
<td>838</td>
<td>50.3</td>
<td>53.6</td>
</tr>
</tbody>
</table>

Compact tension, referred to as C(T), specimens were machined from the plate by wire electronic discharge machining (EDM) following the dimensional specifications outlined in ASTM E647-05. The samples were extracted from the plate in the L-T orientation so that the cracks would grow perpendicular to the longitudinal rolling direction. As shown in Figure 12, the nominal thickness of the specimens (dimension “B”) were machined to 5.84 ± 0.127 mm (0.230 ± 0.005 in) and the notch was machined to a size of a/W = 0.2.

![C(T) specimen geometry](image)

Figure 12. C(T) specimen geometry (all dimensions in inches).
3.2 Constant ΔK and K Crack Growth Tests

The configuration of the retort chamber and DCPD system used to control environmental conditions and measure crack lengths will described in this subsection. Also, the mechanical testing procedures will be outlined.

3.2.1 Experimental Setup

A retort/furnace system specially constructed for this experiment was used in all tests and is shown schematically in Figure 13. The system allowed measurement of temperature and oxygen concentration of the bulk gas flowing through the retort chamber. Additionally, oxygen potential was measured directly adjacent to the specimen surface using a Yitria stabilized zirconia oxygen probe. The oxygen probe also contained its own thermocouple to facilitate calculation of the oxygen potential via the Nernst equation. Two thermocouples measured the temperature of the atmosphere in the vicinity of the C(T) specimen: one sheathed K-type thermocouple which also fed back into the temperature controller and one R-type thermocouple attached to ZrO₂ oxygen probe. A thermocouple could not be directly welded to the surface of the C(T) specimen due to interference between the direct current potential drop (DCPD) measurement technique that was used and the thermocouple reading. However, a third thermocouple was welded to the Alloy 718 pin/grip assembly as close as possible to the C(T) specimen. The three temperature measurements allowed control within ±3°C. The test specimen was electrically insulated from the pins and grips by placing ZrO₂ hollow cylinders around the pins used to hold the specimen and washers between the grips and specimen. Since the sample was “enveloped” by the gripping system it is very unlikely that a significant difference existed between the sample temperature and the grip/pin near the sample. It is also unlikely that resistance heating of the sample was significant. During DCPD development, calibration runs of the system were carried out on samples outside the furnace. No significant increase in sample temperature was observed when 2 A of current was applied to the sample (note: DCPD measurements in actual tests were performed in current control mode at 2 A). Subsequent simultaneous measurement of both the sample and the grip temperatures showed that the temperature difference between the two locations was essentially zero.
Figure 13. Schematic of experimental setup for constant $\Delta K$ and $K$ crack growth tests.

In addition to the retort system, a custom suite of software was written in Visual Basic to control the overall system and to facilitate the measurement of crack growth using the DCPD technique. A schematic of the control system and DC potential drop setup is shown in Figure 14. The system is fully computer controlled and used a reversing DCPD method for the measurement of crack length. The PC serves the purpose of setting up the instruments for the DC potential drop measurement, recording the DCPD values along with environmental variables (temperature, oxygen partial pressure, etc.), and communicating with the Instron load frame controller. This control system allows for testing at constant $\Delta K$, constant $K$, variable $dK/da$ as well as conventional fatigue loading.

To calculate crack length via a potential drop measurement, the ASTM E647-05 standard suggests using a second reference C(T) specimen. This reference specimen is to be exposed to the same environment as the test specimen with the exception of mechanical loading, and use a correlation between the test specimen/reference specimen potential and crack length. However, a reference specimen could not be used due to space restrictions within the retort. Instead, a
closed form DC potential drop fit equation developed by Andresen at GE (Appendix C) was used, which is valid for an a/W range of 0.38 to 0.75. The final precrack length was measured under load with 0.01 mm accuracy using a dial gauge mounted on optical microscope. When the sample was set up in the retort system and the temperature and chemistry had equalized, approximately 80% of the initial testing load was applied. The final precrack length was then entered into the Visual Basic program and a correlation between the measured potential drop voltage and the visual precrack length was calculated. This initial measured DC potential value was used for all subsequent measurements and essentially served as the reference specimen.

The DCPD measurement system was run in current control mode at 2 amperes. Two separate potential measurement channels were used with each channel having contacts welded at opposite corners of the machined crack mouth opening. To average out any electromagnetic and temperature variations, four total readings were taken for each potential drop measurement: two readings corresponding to each set of potential leads (2 channels) and two more readings with the current polarity reversed. These four readings were then averaged and recorded as one potential drop measurement. When a fixed number of potential drop measurements were recorded (number defined by the operator), the values within one standard deviation of the mean were averaged and a data point was recorded in the data file. For sinusoidal loading above 1 Hz,
the program uses an analog trigger generated by the Instron controller to take the potential measurements at the peak maximum of the waveform which compensated for any crack closure effects. A data point is recorded to the data file approximately every 1.5 minutes. Below 1 Hz, the program continuously takes data along the waveform and a data point is recorded approximately every 3 minutes.

3.2.2 Mechanical Testing Procedures

Before testing, all specimens were precracked at room temperature with a loading frequency of approximately 25 Hz and load ratio \(\frac{P_{\text{max}}}{P_{\text{min}}}\) of 0.1 up to a minimum \(a/W = 0.38\). Also, careful consideration was given to the \(\Delta K\) applied to the specimens during precracking so that it would not exceed the values used in actual testing.

During all tests, a temperature of \(650 \pm 3^\circ\text{C}\) was maintained inside the retort. Fatigue tests were conducted under constant \(\Delta K\) (within each step of the test sequence) with a load ratio of \(R = 0.1\) and 0.5. Furthermore, the frequency for the sine wave loading cycle was chosen to be either 0.1 or 2 Hz. The oxygen potential in the retort was controlled using premixed gas mixtures of 10, 50 and 1000 vppm \(\text{O}_2\) with argon. Furthermore, tests were also run in inert conditions which were achieved by running ultra-high purity argon run through a gettering furnace. This was found to produce lower oxygen partial pressures than evacuating the retort with a turbo pump.

The DC potential drop method was valid over the \(a/W\) range 0.38 to 0.75 so that various \(\Delta K\) variations and frequency changes could be made for each specimen. However, higher \(\Delta K\) values induce a larger plastic zone ahead of the crack tip so the test sequence was set up so that the \(\Delta K\) value was either maintained constant or increased during the course of the test. This was to ensure the crack tip was not located within the plastic zone formed by a higher loading amplitude, as this could cause the crack growth to slow or even stop.

3.3 Fracture Surface and Grain Boundary Analysis

Samples were analyzed using various electron microscopy systems. A TOPCON ABT-150 scanning electron microscope with a LaB\(_6\) filament was used mainly for surface inspection. To view fracture surfaces after testing, the C(T) specimen were fatigued for approximately \(1 \times 10^5\) cycles at room temperature to well define the ending point of crack growth under test conditions.
After enough crack growth had occurred during fatigue, the C(T) specimen were pulled apart entirely to create two halves. The electron beam could then be perpendicular to the intergranular/transgranular fracture surface.

Grain boundary visual and compositional analysis was performed ahead of crack tips using high resolution scanning electron microscopy and Auger spectroscopy (AES). Since the C(T) samples could not be further stressed after testing to preserve the crack tip region, they were instead sectioned by wire EDM midway through their thickness (approximately 2.92 mm (0.115 in) in dimension B in Figure 12) to produce two identical sections which permitted a side view of the grain boundaries the crack was following. The surface corresponding to the middle of the full width C(T) specimen was then polished using only diamond grinding and polishing compounds to a 0.25 µm finish. Note that silica and alumina final polishes could not be used for the standard final polish since they leave a tenacious surface film that would interfere with the Auger spectroscopy analysis. Visual inspection of the grain boundaries were performed using FEI/Philips XL30 field emission gun ESEM equipped with a solid state backscatter detector. Optimum surface sensitive imaging conditions were achieved at lower accelerating voltages (~10 kV) with the backscatter electron detector, not the primary secondary electron detector. The AES was performed using a Physical Electronics Model 700 Scanning Auger Nanoprobe which is capable of good elemental sensitivity (1.0 to 0.1 at. %) and high lateral resolution (minimum 6 nm). Regions in which analysis was performed were cleaned in the ultra-high vacuum analysis chamber using an ion gun to remove any absorbed or surface layer contaminants. The compositional information was mainly obtained from point analyses, line scans, and compositional maps.
4. RESULTS

4.1 Microstructure and Grain Size

INCONEL Alloy 617 is a solid-solution strengthened alloy in which the strengthening is mainly imparted by cobalt and molybdenum. Some additional strengthening may be provided by carbides, primarily chromium-rich $\text{M}_{23}\text{C}_6$ and molybdenum-rich $\text{M}_6\text{C}$ types. Figure 15 shows a 3-D reconstruction of the microstructure of the as-received alloy plate. Note that each of the

![Figure 15. Three-dimensional reconstruction of Alloy 617 microstructure at 100x. Surfaces have been electrolytically etched at 8V for 25s in a 7.8% perchloric acid solution.](image)
three images used to make the 3-D reconstruction was taken from a different section of the plate and then mapped onto the surface of a cube. Any correlation of grain boundaries at the edges is coincidental. The figure shows bands of carbide stringers aligned in the rolling direction formed during processing (i.e. rolling) of the plate. Regions of fine grain structure are associated with the carbide stringers whereas a coarse grain structure is noticeable in the regions free from carbides. Since the alloy exhibits a duplex grain size distribution, grain size measurements were taken separately in the coarse and fine grain regions. Coarse grains have an ASTM grain size number of 4.4, corresponding to an estimated spatial diameter of 108 ± 9.3 μm. The finer grains have an ASTM grain size number of 7.2, corresponding to an estimated spatial diameter of 41.8 ± 2.7 μm.

To compare the microstructure of the alloy after a test, one of the samples was electrolytically etched (under the same conditions as the as-received material) after ~750 hours at 650°C. Figure 16 shows the comparison of the microstructures in the LT-RD plane. This is the only direction that could be compared since the C(T) specimen did not have enough exposed area on the other two perpendicular planes. No significant difference is seen in the grain size distribution between the two microstructures. Grain size measurements of the post-test material obtained an ASTM grain size number of 6.7, corresponding to an estimated spatial diameter of 49.6 ± 4.1 μm. However, the post-test microstructure did not exhibit a pronounced duplex structure like the as-received microstructure. The carbide network is more continuous and many more fine carbide particles are visible in the material after testing in Figure 16. Similar microstructural characteristics are described in an aging study conducted at 648°C for 1000 hr on Alloy 617 [62]. Since these properties would only serve to strengthen the material, evolution of the microstructure during testing at 650°C was not a concern.

4.2 Crack Growth Tests

4.2.1 Constant ΔK Fatigue Crack Growth

Fatigue tests were performed at 650°C under constant ΔK at different oxygen partial pressures, frequencies, and load ratios. All samples were tested at two different loading frequencies: 0.1 and 2 Hz. The gas environment was held constant during each fatigue test and changed from sample to sample. After steady crack growth rates were achieved for both frequencies under
Figure 16. Comparison of microstructures at 50x magnification in the as-received condition (top) to microstructure after testing for ~750 hr at 650°C (bottom). The long transverse direction is along the x-axis and the rolling direction along the y-axis.
constant ΔK conditions, the stress intensity factor range was increased to achieve different crack growth rates. Figure 17 shows a typical data set for the entire test sequence of the specimen tested at an oxygen partial pressure of 9.71x10^{-4} atm (1000 vppm O₂ in Ar mixture). Since the crack growth rate da/dN is proportional to the stress intensity factor range, the crack growth rates do increase as expected as the stress intensity factor is increased. For each test, the crack growth rates for each ΔK and frequency combination were calculated using a linear least squares regression. These results are compiled on a crack growth rate vs. stress intensity factor range log-log plots. Under the same stress ratio, the crack growth rates plotted against stress intensity factors on a log-log scale should increase nearly on a straight line.

Figure 18 and Figure 19 plot da/dN vs. ΔK for R = 0.1 for two different gas environments. One specimen was tested in high purity argon gas during which the oxygen sensor measured the partial pressure of oxygen to be at most 10^{-12} atm. The second specimen was tested in a mixture of oxygen/argon gas rated at 1000 vppm oxygen in which the partial pressure of oxygen was

![Crack length versus the number of cycles showing the transition in crack growth rates in a standard test sequence. Test conditions were R = 0.1 and a gas environment of 1000 vppm O₂ in argon.](image-url)
measured to be approximately $9.71 \times 10^{-4}$ atm. As expected, the crack growth rates for each oxygen partial pressure and frequency value exhibit a nearly linear response with increasing $\Delta K$ values on the log-log scale. Furthermore, the behavior of the crack growth rates in relation to the fatigue frequency should be noted. At lower frequencies, it is likely that the oxygen will have more time to interact with the alloy near the crack tip and thus allow for more extensive oxide formation or embrittlement before it is broken in tension in the subsequent cycle. This would lead to higher crack growth rates. In Figure 19, the crack growth rates are slightly higher at a frequency of 0.1 Hz than at a frequency of 2 Hz except for a $\Delta K$ of $\approx 35$ MPa/m. This could indicate that fatigue crack growth at 0.1 Hz and high oxygen potentials (i.e. 1000 vppm $O_2$ in Ar) is a partly time dependent process. The 2 Hz data may also exhibit a time independent regime although not enough frequencies were tested in this study to determine where this cutoff occurs. Previous data for Alloy 617 tested at 650°C in air shows that the cutoff between time independent/dependent fatigue crack growth usually occurs around a frequency of 0.5 Hz [63]. Figure 18 shows no discernable pattern when comparing the 0.1 and 2 Hz data. For the data in this figure, the oxygen partial pressure was less than $10^{-12}$ atm ($10^{-6}$ vppm $O_2$ in Ar) in the retort so embrittlement and/or oxidation processes in this case may be insignificant to crack growth rates in the $10^{-6}$ to $10^{-7}$ m/s range.

Figure 20 and Figure 21 plot the same data shown in Figure 18 and Figure 19 except that the data in each plot are now shown with the same mechanical loading conditions (i.e. load ratio and frequency). This assists in showing the difference in fatigue crack growth with the only variable being the oxygen partial pressure. Both of these figures illustrate a discernable increase in growth rate for the higher oxygen potential at each $\Delta K$ value indicating an effect of oxygen potential on fatigue cracking. The data points at approximately 40 MPa/m in Figure 21 are the only two which do not follow this trend. Looking more closely at the trend of data points for which the oxygen partial pressure was less than $10^{-12}$ atm in this figure, the response to increasing the $\Delta K$ value is irregular compared to the nearly linear response of the data for the other oxygen potential. During the fatigue test in which the oxygen potential was at most $10^{-12}$ atm, the oxygen potential was actually continuously decreasing as the test progressed due to bake-out of absorbed oxygen on retort walls, sample grips, etc. This means that as the $\Delta K$ values were increased, the oxygen potential was decreasing so that the measured oxygen potential during the crack growth at 40 MPa/m was approximately $1.4 \times 10^{-20}$ atm. The stability of nickel
Figure 18. Fatigue crack growth rate vs. the stress intensity factor range with $R = 0.1$ and $P_0 < 10^{-12}$ atm.

Figure 19. Fatigue crack growth rate vs. the stress intensity factor range with $R = 0.1$ and $P_0 = 9.71 \times 10^{-4}$ atm.
Figure 20. Fatigue crack growth rate vs. the stress intensity factor range with $R = 0.1$ and 0.1 Hz loading.

Figure 21. Fatigue crack growth rate vs. the stress intensity factor range with $R = 0.1$ and 2 Hz loading.
oxide at this temperature is very close to this oxygen potential. The dissolution of the nickel oxide film at the crack tip could explain why the data points at ~40 MPa√m show the crack growth rate tested in argon as being higher than the crack growth rate for the sample tested at $P_o = 9.71 \times 10^{-4}$ atm (1000 vppm O₂ in Ar).

A second set of samples was tested at a load ratio of R = 0.5 in four different environments: high purity argon and 10, 50, and 1000 vppm O₂ in argon. Again, the environment was held constant during each test while the frequency and $\Delta K$ values were changed. Figure 22 shows the results of the test conducted in high purity argon gas in which the maximum oxygen partial pressure was measured at approximately $10^{-21}$ atm. Note that the oxygen concentration reached a minimum value of approximately $7 \times 10^{-22}$ atm, so the environment in this test fluctuated minimally compared to the fatigue test conducted at R = 0.1 in argon. Again, the trend is a nearly linear increase in crack growth rate with increasing $\Delta K$ values. Furthermore, the data at 0.1 Hz is consistently higher than the 2 Hz data, indicating that crack growth is at least partially time dependent even at very low oxygen potential. Figure 23, Figure 24, and Figure 25 plot the data in 10, 50, and 1000 vppm O₂, respectively. The partial pressure of oxygen for the 10, 50, and 1000 vppm O₂ environments was measured to be approximately $9.44 \times 10^{-6}$, $4.82 \times 10^{-5}$, and $9.46 \times 10^{-4}$ atm, respectively. Similar to Figure 22, the crack growth rates for the environments containing oxygen show nearly linear responses in crack growth rates on a log-log plot. The only inconsistency is seen in Figure 24 where the crack growth rates at approximately 19.2 and 22 MPa√m and 2 Hz where the values are much lower than expected. However, the data at 16.5 and 24.7 MPa√m with 2 Hz loading are more congruent with trends seen in Figure 22, Figure 23, and Figure 25. In particular, the difference of the crack growth rates between the 0.1 Hz and 2 Hz at $\Delta K = 16.5$ and 24.7 MPa√m conforms more to the trends seen in the differences between 0.1 Hz and 2 Hz growth rates for other oxygen concentrations.

To illustrate the effect of oxygen partial pressure in the data where R = 0.5, the data points tested at the same frequencies are grouped together on crack growth rate vs. $\Delta K$ log-log plots in Figure 26 and Figure 27. Both of these figures again show an increase in growth rate for the higher oxygen concentrations. More specifically, the crack growth rates at $P_o = 9.46 \times 10^{-4}$ atm (1000 vppm O₂ in Ar) are clearly higher than the growth rates at the other oxygen concentrations.
Figure 22. Fatigue crack growth rate vs. the stress intensity factor range with $R = 0.5$ and $P_o < 10^{-21}$ atm.

Figure 23. Fatigue crack growth rate vs. the stress intensity factor range with $R = 0.5$ and $P_o = 9.44 \times 10^{-6}$ atm.
Figure 24. Fatigue crack growth rate vs. the stress intensity factor range with $R = 0.5$ and $P_0 = 4.82 \times 10^{-4}$ atm.

Figure 25. Fatigue crack growth rate vs. the stress intensity factor range with $R = 0.5$ and $P_0 = 9.46 \times 10^{-4}$ atm.
Furthermore, Figure 26 visibly demonstrates an increase in the rates tested in $P_{O_2} = 9.46 \times 10^{-4}$ atm over the rates in $P_{O_2} = 4.82 \times 10^{-5}$ atm. However, the difference in between growth rates for the lower oxygen concentrations, $P_{O_2} < 10^{-21}$ atm and $P_{O_2} = 9.44 \times 10^{-6}$ atm (10 vppm O$_2$ in Ar), does not follow a clear pattern. Since the growth rates at these low oxygen concentrations is negligible in Figure 26 and most likely within the error of the crack growth measurement, it would unreasonable to make a statement that the growth rates at an oxygen partial pressure of $9.44 \times 10^{-6}$ atm are higher than those at $P_{O_2} < 10^{-21}$ atm. The overall trend for the crack growth rate to increase with increasing oxygen potential at each $\Delta K$ value does again conform with the literature [63] as the crack growth is expected to be subject to time dependent environmental processes for 0.1 Hz loading. Figure 27 further demonstrates that when 2 Hz loading is employed, the growth rates at $P_{O_2} = 9.46 \times 10^{-4}$ atm are still consistently higher than the other concentrations, meaning that environmental processes are still important even for higher frequencies. However, the rates at the lower three oxygen concentrations are insignificant.
and two outlying points at approximately 19.2 and 22 MPa√m for $P_{O_2} = 4.82 \times 10^{-5}$ atm make any comparisons more obscure. Overall, this could point towards changes inherent in the material (such as carbide or grain size dispersion) as becoming more prevalent and responsible for changes in crack growth rates at higher fatigue frequencies. In comparing the differences between Figure 26 and Figure 27, the data suggests that some of the environmental effect on crack growth has been overtaken by mechanical or other processes as the frequency is increased. While the highest oxygen concentration at 2 Hz still allows for environmental interaction at the crack tip, increasing the fatigue frequency higher should eventually remove all environmental and time-dependent processes to the point where there would be no differences in growth rates at different oxygen concentrations. This higher frequency fatigue regime was not explored in this study since crack growth rates under static loading and changing oxygen concentrations were more crucial to this research.
4.2.2 Static Loading (constant K) Crack Growth

Figure 28 shows the results of the static crack growth behavior for material tested under constant K conditions (49.5 MPa√m) as a function of oxygen potential. The data is plotted as crack length (solid line) vs. time on the left vertical axis and also the corresponding oxygen concentration changes (dotted line) with the oxygen partial pressure scale on the right vertical axis. As seen in the smaller crack growth rate vs. oxygen partial pressure plot, unlike the fatigue behavior seen in the previous section, the crack growth rate increases as the oxygen concentration decreases over the range of oxygen concentration tested. The results shown in

![Diagram showing crack growth vs. time and oxygen partial pressure](image)

Figure 28. Large plot shows crack growth vs. time at $K = 49.5$ MPa√m under static loading conditions. The smaller crack growth rate vs. oxygen partial pressure plot in the upper left corner illustrates the decrease in growth rates as the oxygen concentration is increased.
Figure 28 were conducted on a sample that had already undergone a series of fatigue crack growth steps before it was put into static loading. Unfortunately, the stress intensity ratio used for these results, $K = 49.5 \text{ MPa}^{\frac{1}{2}}$, did not meet the requirement for the specimen’s uncracked ligament size to be met according to section A1.2.6.1 in the ASTM E647 standard. While it is expected that the final design of the NGNP will comply with all ASME codes and standards, stresses at existing flaws (due to materials processing and component construction), in general, will preclude high stress intensity factors. However, due to unforeseen local stresses during operation, most likely in thick sections where thermal gradients may exist or during life where existing flaws have grown and gone undetected, the local stress intensity may become very high. Since the above behavior is different than that at a lower stress intensity factor (discussed next), it was important that the possibility of operating at $K = 49.5 \text{ MPa}^{\frac{1}{2}}$ be considered and that data in this regime be noted and discussed. Also for these reasons, more controlled tests were employed to obtain static loading crack growth at lower stress intensity values.

Three specimens were tested under static loading conditions at $K = 33.0 \text{ MPa}^{\frac{1}{2}}$ to test the effect of varying oxygen potential on crack growth rates. The lower stress intensity factor chosen for these three specimens allowed for the uncracked ligament size criteria in ASTM E647 to be fulfilled over the entire crack length tested. Furthermore, unlike the previous static loading test in which the environment was simply varied for one specimen under static crack growth conditions, three data points were obtained from three separate tests. To avoid crack arrest when the static load was applied under these conditions, a series of loading steps was utilized in which successive fatigue loading steps had decreased frequencies and increased stress ratios. The last step before static loading applied a trapezoidal waveform with a 500s hold time at maximum load and $R = 0.875$. The static crack growth rates with varying oxygen partial pressure results shown in Figure 29. There is very little change in crack growth rates to increasing oxygen potential with all of the data residing in the range of approximately $9 \times 10^{-11}$ to $10 \times 10^{-11} \text{ m/s}$. This result differs from the previous findings on static crack growth rate sensitivity to oxygen at $K = 49.5 \text{ MPa}^{\frac{1}{2}}$. The data point from the test conducted in gettered argon obtained an extremely low oxygen partial pressure, $P_{o_2} \approx 5 \times 10^{-22} \text{ atm}$ as noted by the large break on the x-axis in Figure 29. The test conducted in argon in the static loading test at $K = 49.5 \text{ MPa}^{\frac{1}{2}}$ only obtained an oxygen partial pressure of approximately $5 \times 10^{-7} \text{ atm}$. 

53
Figure 29. Crack growth rate vs. oxygen partial pressure for static loading at $K = 33.0$ MPa$\sqrt{m}$.

### 4.3 Fractography

The sample in which testing ended under static loading conditions at $K = 45$ MPa$\sqrt{m}$ (the crack growth rates for this sample are shown in Figure 28) was inspected using scanning electron microscopy. As shown in Figure 30, the crack path shifts from transgranular to intergranular fracture when the loading mode is changed from cyclic to static. This micrograph shows a large fraction of transgranular fracture generated at the beginning portion of the test and the immediate transition when a short static loading step was implemented. After this long period of fatigue fracture followed by a short static loading step, the sample was again put under fatigue loading during the test sequence and finally ended under another short static loading step. To preserve the crack tip region of the sample, the first section which fractured under fatigue loading was cut away on one side of the crack opening. Looking closely at the very left edge of Figure 31 above the open crack, the cut used to image the section of fracture surface in Figure 30 can be seen. This second transition from fatigue to static loading is shown in Figure 31 with the specimen oriented side-on and graphically portrays the change in crack path/morphology. The transition is
accompanied by extensive grain boundary cracking away from the immediate crack tip as well as extensive branching. In Figure 32, part of the intergranular crack opening is shown at higher magnification. The faceted fracture surface is clearly distinguishable from the smoother transgranular features. Also, one of the regions of intergranular cracking away from the immediate crack tip is shown at higher magnification in Figure 33. The damage seen on the surface could be interconnected through crack branching below the specimen surface. If this is the case, the crack branching would most likely be detected by the DCPD measurement as an increase in crack length. This extensive damage on the surface may be due to the high stress

![Fatigue - Static](image)

![Crack Propagation](image)

**Figure 30.** Scanning electron micrographs of typical fracture surface. The transition from fatigue to static loading is shown at a higher magnification in the latter micrograph and demonstrates a clear interface between transgranular and intergranular failure.
intensity factor to which this specimen was subject to upon completion of crack growth. Since the amount of uncracked ligament in the sample had already failed to meet the requirement in the ASTM E647 standard, the sample was not sectioned through its thickness to determine the extent on the damage.

Figure 31. Scanning electron micrograph of specimen oriented edge-on to show transition between fatigue and static loading. Also shown is the crack tip region.

Figure 32. Secondary electron image taken inside the intergranular fracture regime of Figure 31 showing a clearly faceted intergranular fracture surface.
Figure 33. SEM image taken at 2500x showing extensive intergranular crack branching.

Figure 34 and Figure 35 show two high resolution images taken at the crack endpoints of static loading tests which ended under $P_{o_2} = 9.29 \times 10^{-4}$ and $P_{o_2} = 4.57 \times 10^{-5}$ atm, respectively. Both of the images clearly show the crack propagation mode was intergranular fracture. Some intergranular fracture is also apparent in Figure 36 where a secondary crack branch terminated in a region occupied by many carbides (note: this image was taken from the same specimen as Figure 34). Furthermore, the right crack branch in Figure 34 and main crack in Figure 35 show the crack tip terminating at grain boundary triple point junctions. A closer examination of the grain boundaries in Figure 34 reveals that there may be some intergranular cavitation for a region approximately 25 µm in diameter directly ahead of the crack tip. In contrast, Figure 35 shows very little cavitation at the magnification of the micrograph. Three final comments on the microstructure should be noted even though they are not related to the fractography of the specimens. Blocky carbides can been seen randomly dispersed through the matrix with sizes varying widely from approximately 0.5 to 2.0 microns in diameter. The more common of these carbides appears to be the chromium rich type which have a darker contrast as seen in Figure 36 and Figure 37. It was verified that these darker contrast carbides are chromium rich through the Auger spectroscopy analysis presented in the next section. Figure 35 also shows some very light contrast particles which appear spherical from a distance but at higher magnifications show the
same blocky structure of the chromium carbides. The second point regarding the microstructure is in regard to small intergranular particles visible in both micrographs and also shown at higher magnification in Figure 37. The particles range in size from approximately 200 to 400nm and there appears to be both light and dark contrast particles in the BSE image indicating compositional variation. From optical microstructural observations and subsequent Auger spectroscopy analysis, the particles were identified as chromium and molybdenum rich intergranular carbides. Finally, large compositional variation can be seen throughout the matrix, especially in Figure 34. These fluctuations in composition are smaller in magnitude than the grain size and do not show any directionality, so it is most likely the result of alloy processing. This microstructural variation will be taken into account when considering the results of the Auger spectroscopy analysis.
Figure 34. Backscatter scanning electron micrograph taken at 1000x of a sample completed under static loading conditions at $K = 33.0$ MPa$\sqrt{m}$ and $P_{O_2} = 9.29 \times 10^{-4}$ atm (~1000 ppm O$_2$ in Ar) showing two end points of intergranular cracks and intergranular cavitation further along the grain boundaries.
Figure 35. Backscatter scanning electron micrograph taken at 1000x of a sample completed under static loading conditions at $K = 33.0$ MPa$\sqrt{\text{m}}$ and $P_{O_2} = 4.57 \times 10^{-5}$ atm (~50 ppm O$_2$ in Ar) showing the intergranular fracture surface ending at a triple point junction.
Figure 36. Backscatter electron image showing a crack which traversed through a heavily carbided region which are distinguishable from the matrix by their faceted structure. The light and dark carbides are molybdenum and chromium rich, respectively.

Figure 37. A small region taken from Figure 35 showing chromium rich carbides dispersed through the matrix and also both light and dark contrast particles on the grain boundaries.
4.4 Composition and Grain Boundary Analysis

Analysis of composition changes were obtained using high resolution Auger electron spectroscopy (AES), which allowed for approximately an order or magnitude increase in sensitivity over standard SEM analytical techniques such as energy dispersive spectroscopy (EDS). Furthermore, the Auger electrons can only escape from very near the surface of the electron beam interaction volume. This has both advantages and disadvantages for the purposes of examining the composition since samples needed to be polished well enough to ensure an atomically clean and nearly flat surface. After polishing, an ion gun was used in the ultrahigh vacuum Auger spectroscopy chamber to further clean of any surface contamination or absorbed atoms which may have simply resulted from sample transport or short exposure to the lab environment. After the surface has been sputter cleaned, the very near surface sensitivity becomes advantageous. Any features visible on the surface with the secondary electron detector have the possibility of being analyzed for compositional variations without having to account for information coming from neighboring areas far below the surface. The x-ray escape for EDS usually on the order of microns and would clearly not give the resolution necessary to give analytical information adjacent to the grain boundaries.

Only two samples ending under static loading conditions were able to be analyzed via Auger spectroscopy. The first sample, designated 617-UK-02, was finished testing under static loading at \( K = 30 \text{ MPa/m} \) and \( P_{O_2} = 9.46 \times 10^{-4} \text{ atm} \) (~1000 vppm \( O_2 \) in Ar). The second sample, designated 617-UK-12, was completed under static loading at \( K = 30 \text{ MPa/m} \) and \( P_{O_2} = 4.82 \times 10^{-5} \text{ atm} \) (~50 vppm \( O_2 \) in Ar). The results for these two specimens will be divided into the two sections.

4.4.1 Results for 617-UK-02: \( K = 30 \text{ MPa/m}, P_{O_2} = 9.46 \times 10^{-4} \text{ atm} (~1000 \text{ ppm } O_2 \text{ in Ar}) \)

The fractured region shown in the backscatter electron image in Figure 36 which is occupied by carbides adjacent to both sides of the crack was analyzed by a compositional mapping and an Auger survey analysis. The exact area used for the compositional map is shown in Figure 38 and the compositional mapping results are shown in Figure 39. The mapping results indicate that the darker regions in Figure 38 are chromium rich carbides and the lighter regions are molybdenum rich. Furthermore, the results show that both types of carbides have small amounts of nickel.
present although in different amounts. To further clarify this point, Figure 40 shows the areas in which a survey analysis was conducted to determine the percentages of elements in both types of carbides and the surrounding matrix. The compositional results in Table 3 indicate that the molybdenum rich carbides contain a slightly higher amount of nickel although not nearly as high as the surrounding matrix. The intensities of both oxygen and carbon in Figure 39 should also be discussed. As expected, the fractured surface shows an increase in oxygen concentration which could have resulted from either newly exposed surfaces oxidizing subsequent to fracturing or an oxide film (or oxidized particle) on the grain boundary ahead of the crack tip rupturing under load. The surrounding molybdenum rich carbides also have a slightly higher concentration of oxygen present than in the surrounding matrix. Finally, the carbon intensity at the fracture surface shows a large increase in intensity. Since the sample needed to be polished after being sectioned, diamond suspensions were used during preparation. These diamond particles (0.25 μm in the last polished step) most likely were still trapped within the fracture surface even though the sample was thoroughly cleaned.

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1 Please note that the survey analysis scans through the whole Auger energy spectrum (i.e. all elements), but only certain peaks are chosen from the spectrum for analysis purposes. In Alloy 617, some secondary and tertiary peaks for elements present in high percentages directly overlap the peaks for other alloying elements such as cobalt (secondary nickel peak coincidence), aluminum, and iron. Furthermore, compositional percentages of each element cannot be determined on an absolute basis. The percentages for the elements which are chosen for the survey analysis will sum to 100%.
Figure 39. Compositional mapping results of a cracked region occupied by Cr and Mo carbides. Note that an increase in intensity of an element is marked by an increase in brightness in the above images.
Figure 40. Secondary electron image showing the three survey analysis regions taken from the carbide region: 1) matrix adjacent to carbides 2) chromium rich carbide 3) molybdenum rich carbide.

Table 3. Survey analysis results of the three regions analyzed in Figure 40. Note that the results are in percentages for each element and are not absolute values, meaning each region must sum to 100%.

<table>
<thead>
<tr>
<th>Region</th>
<th>C1 %</th>
<th>Cr2 %</th>
<th>Ni1 %</th>
<th>Mo1 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>46.06</td>
<td>15.79</td>
<td>33.37</td>
<td>4.78</td>
</tr>
<tr>
<td>2</td>
<td>58.96</td>
<td>30.09</td>
<td>3.36</td>
<td>7.60</td>
</tr>
<tr>
<td>3</td>
<td>58.25</td>
<td>10.54</td>
<td>10.72</td>
<td>20.48</td>
</tr>
</tbody>
</table>

For this sample, the first analysis of the crack tips and grain boundaries consisted of a survey analysis with three areas as shown in Figure 41: one area positioned on the matrix adjacent to the fracture, another area positioned within the fracture, and the final area ahead of the fracture on the grain boundary. The end point which was analyzed is from the branch on the right hand size of Figure 34. Looking at the results in Table 4, there are major differences between the matrix
and Region 2 within the fracture zone. As seen in the mapping results, a large increase in oxygen is observed inside the fracture. There are also significant decreases in nickel and molybdenum between the matrix and the fractured surface. However, the difference in carbon concentrations between the two regions is negligible and the decrease in chromium is not nearly as severe as it is for both nickel and molybdenum. This would likely indicate that a chromium rich oxide is forming at the fracture surface. The differences between region 3 ahead of the crack tip and the matrix show depletion in oxygen. This decrease in oxygen may be explained by the small increase in carbon and molybdenum concentration in this region if a molybdenum rich carbide formed on or near the grain boundary. There is a possibility the depletion in oxygen is also the result of a preferential reaction between oxygen and a carbide.

To further elucidate the changes of compositions on the grain boundary, two line scans were performed ahead of the crack tip on the left hand side of Figure 34. This branch was chosen for

Figure 41. Image showing the three survey analysis regions taken near a crack tip in which the specimen was tested with $K = 30 \text{ MPa m}^{-1/2}$ and $P_{O_2} = 9.46 \times 10^{-4} \text{ atm} \,(\sim 1000 \text{ ppm } O_2 \text{ in Ar})$. Description of each region as follows: 1) matrix far from crack 2) inside fracture surface 3) on grain boundary ahead of crack.
Table 4. Survey analysis results of the three regions analyzed in Figure 41.

<table>
<thead>
<tr>
<th>Region</th>
<th>Cl %</th>
<th>O1 %</th>
<th>Cr2 %</th>
<th>Ni1 %</th>
<th>Mo1 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.60</td>
<td>7.57</td>
<td>29.62</td>
<td>42.95</td>
<td>13.26</td>
</tr>
<tr>
<td>2</td>
<td>6.58</td>
<td>60.84</td>
<td>23.18</td>
<td>6.02</td>
<td>3.38</td>
</tr>
<tr>
<td>3</td>
<td>8.43</td>
<td>3.30</td>
<td>24.42</td>
<td>49.30</td>
<td>14.56</td>
</tr>
</tbody>
</table>

further analysis since the crack tip and grain boundary were better defined. The first line scan was placed approximately 3 to 4 μm ahead of the final visible crack opening as shown in Figure 42. The grain boundary which is approximately perpendicular to the analysis line reveals some darker regions have formed adjacent to both sides of the boundary. The thickness of these particles on the grain boundary is on the order of approximately 100 nm so they cannot be part of the grain boundary structure itself. The results of the line scan shown in Figure 43 indicate that there is a large increase in chromium and depletion in oxygen and nickel in the region of the grain boundary. The carbon intensity was not analyzed for this line scan but previous results in Table 4 and the results for the next line scan suggest that these dark particles along the grain boundary are chromium carbides. The second line scan for this sample was performed approximately 5 μm further away from the crack tip on the same grain boundary. This region is shown in Figure 44 and again the grain boundary is in the middle of the image approximately perpendicular to the analysis line. On the far left side of the figure, the analysis line intersects another particle which is similar in size and gray tone as the dark particles in Figure 42. Reviewing the line scan results in Figure 45, an increase in chromium and a decrease in nickel and oxygen is again observed. The changes in intensity of these elements are the same across the particle on the far left side and the particle on the grain boundary. Also, the carbon intensity was scanned in this analysis and shows the same increase on the both particles. This validates the previous statement that these particles are indeed chromium carbides.

For the final analysis of this sample, the compositional map was taken in the region shown in Figure 46. This region is in approximately the same area as the first line scan and also just beyond the visible fracture surface for this branch of the crack. The grain boundary region is populated by carbides seen in the previous line scans and there are some significantly smaller
Figure 42. Image showing the analysis line traversing a grain boundary ahead of a crack in which resulted from loading at \( K = 30 \) MPa\(\sqrt{m} \) and \( P_{O_2} = 9.46 \times 10^{-4} \) atm

Figure 43. Line scan analysis results of the line shown in Figure 42 revealing an increase in chromium on the boundary and a decrease in both oxygen and nickel.
Figure 44. Line scan performed approximately 5 μm further on the same grain boundary as Figure 42.

Figure 45. Line scan analysis results of the line shown in Figure 44 revealing an increase in chromium and carbon and a decrease in oxygen and nickel on the boundary. The dark particle the line intersects on the left side yields an increase in chromium and carbon indicating a chromium rich carbide.
circular particles randomly dispersed in the matrix. These small circular particles were also seen in Figure 42 and Figure 44 but not discussed. The compositional mapping results for this area are shown in Figure 47. As seen in the previous analyses, the chromium intensity increases for the particles on the grain boundary, as does the carbon intensity. Also observable is the decrease in nickel and oxygen for these particles on the grain boundary. The map of nickel intensity reveals information absent from the two line scans. Neighboring the grain boundary mostly on the left side of the carbides, there appears to be some segregation of nickel towards the boundary. This segregation of nickel becomes less apparent further along the boundary towards the upper part of the image. To further discuss the oxygen map, the intensity is fairly consistent in the matrix except for two geometric features showing depletion in oxygen which are artifacts from previous analyses: the line approximately one-third from the top of the image and the rectangle in the lower half of the image. The line resulted from the line scan in Figure 42 since the prolonged rasterization of the beam in the same area causes carbon to be deposited and oxygen to be depleted on the surface even in ultrahigh vacuum. The molybdenum map shows almost no changes in intensity except for three small spots which are very molybdenum rich, most likely intergranular molybdenum carbides. Finally, the small circular particles dispersed in the matrix only exhibit a sharp increase in carbon with little to no changes in the other elements analyzed.

Figure 46. Image showing an area ahead of a crack which fractured under loading at $K = 30 \text{ MPa}\sqrt{\text{m}}$ and $P_{O_2} = 9.46 \times 10^{-4} \text{ atm}$ (~1000 vppm $O_2$ in Ar). The image corresponds directly to the area in which compositional maps were obtained.
Figure 47. Compositional mapping images of the grain boundary region directly ahead of a crack tip shown in Figure 46.
4.4.2 Results for 617-UK-12, $K = 30 \text{ MPa} \sqrt{m}$, $P_{O_2} = 4.82 \times 10^{-4} \text{ atm} (~50 \text{ ppm O}_2 \text{ in Ar})$

Line scans were the primary technique employed for the analysis of this sample, which was tested at $K = 30 \text{ MPa} \sqrt{m}$ and $P_{O_2} = 4.82 \times 10^{-5} \text{ atm} (~50 \text{ vppm O}_2 \text{ in Ar})$. A baseline line scan across the visibly fractured region was taken approximately 10 $\mu$m away from the grain boundary triple point as shown in Figure 48. Since only a survey analysis was taken directly on the visible fracture surface for the analyses in the previous section, the line scan on this sample served as a basis for the subsequent line scan analyses ahead of the crack tip. The results of the scan are shown in Figure 49 and Figure 50 with the intensities for each element superimposed directly on the secondary electron micrograph from which the line scan was obtained. The intensities of molybdenum and carbon shown in Figure 49 all significantly decrease as the line traverses the darker film which has formed on both sides of the fracture surface. Furthermore, the nickel concentration appears to rise above the average concentration in the matrix as the fracture surface film is approached and then drops off immediately on the film. Looking at the chromium and oxygen concentrations in Figure 50, it becomes clear that the film is oxygen rich.

Figure 48. Micrographs of an oxidized intergranular fracture surface from a sample tested at $K = 30 \text{ MPa} \sqrt{m}$ and $P_{O_2} = 4.82 \times 10^{-5} \text{ atm} (~50 \text{ vppm O}_2 \text{ in Ar})$. The lower magnification image on the left is the backscatter electron image showing where the line scan on the secondary electron on the right was taken.

72
Figure 49. Line scan analysis results showing the nickel, molybdenum, and carbon intensities superimposed on the secondary electron image of the analysis region.

Figure 50. Line scan analysis results showing the chromium and oxygen intensities superimposed on the secondary electron image of the analysis region.
and that the chromium concentration is at about the same level on the fracture surface film as in the matrix. This would indicate that the film on the fracture surface is a chromium oxide, which has been reported previously in the literature [14]. The sharp decrease in chromium and oxygen occurs in the middle of the fracture surface when the electron beam was inside the crack itself.

As a final point, the analysis passes through a particle which appears to be protruding from the surface approximately 0.5 μm to the left of the fracture surface. The molybdenum and oxygen intensities do not change as the line intersects through the particle. However, the nickel and chromium intensities both show a visible increase and the carbon intensity also appears to increase slightly above its average. The previous sample did not show any chromium carbides which were approximately 250 nm in diameter in the regions which were analyzed. However, the optical microstructure of the alloy indicated that there are regions of highly concentrated carbide stringers while other regions showed almost no or very small carbides widely dispersed in the grains. The reason for the increase in nickel on the particle, however, is unclear unless a surface film is forming on the particle or nickel was rejected during precipitation of the chromium rich carbide. Since the resolution of this line scan was not high, there is not enough information to make any definite conclusions.

The flanks of the fracture surface, the small particles intersected by the line scan, and the matrix were analyzed using point survey analyses as shown in Figure 51. Table 5 summaries the results from the survey analysis. Since Point 3 was positioned on the base metal away from the fracture surface, it was used as a baseline for the other two points. Point 1 shows very little change from the base metal, only revealing a small decrease in the nickel, molybdenum, and oxygen concentrations and a similar increase in the level of carbon and chromium. This does not reveal any additional information than that which was obtained in the line scan analysis of these protrusions. Comparing Point 2 to the base metal, the oxygen level increases dramatically and the nickel, molybdenum, and carbon percentages decrease. The change in chromium between the fracture surface flanks and the base metal is negligible. Since the majority of the material at Point 2 consists of chromium and oxygen, the conclusion that chromium oxide forms on the crack flank is confirmed from the previous line scan.
Figure 51. Image showing the three points used to conduct a survey analysis on and near the intergranular fracture surface. Description of each point as follows: 1) one of numerous particles which was visible in a number of SE images 2) directly adjacent to fracture surface on apparent oxide 3) matrix for baseline.

<table>
<thead>
<tr>
<th>Point</th>
<th>Cl %</th>
<th>O1 %</th>
<th>Cr2%</th>
<th>Ni1 %</th>
<th>Mo1 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21.49</td>
<td>13.21</td>
<td>22.19</td>
<td>32.54</td>
<td>10.56</td>
</tr>
<tr>
<td>2</td>
<td>12.39</td>
<td>47.41</td>
<td>21.12</td>
<td>12.54</td>
<td>6.54</td>
</tr>
<tr>
<td>3</td>
<td>17.47</td>
<td>15.67</td>
<td>21.47</td>
<td>33.98</td>
<td>11.41</td>
</tr>
</tbody>
</table>

Having established a baseline line scan across the open crack, several more line scans at a higher resolution (512 as opposed to 256 points) were performed on the grain boundary ahead of the crack tip beyond the triple point. Figure 52 shows the region in which the first set of lines were placed with the first line directly ahead of the crack tip and the second line approximately 2 μm from the crack tip perpendicular to the grain boundary. The surface near the crack tip again shows many of the small sub-micron particles that were analyzed in the previous survey analysis. The two lines were placed so that as few particles as possible were intersected on the line. The results for the line scan are shown superimposed on the corresponding secondary electron image.
Figure 52. Image on the left showing the region the line scan analysis was performed ahead of an intergranular crack. The high magnification image on the right shows the placement of the lines with line 1 directly ahead of the visibly oxidized surface and line 2 on the grain boundary.

micrograph in Figure 53 and Figure 54. Starting with Figure 53, the boundary directly ahead of the crack tip reveals very little information about changes in composition given that the oxygen and carbon show no changes in intensity. There is an increase in the nickel intensity with a corresponding decrease in the chromium intensity directly at the grain boundary. This increase in nickel is similar to the increase in intensity seen on the small particle in Figure 49 and also the steady increase on nickel as the left hand side of the open crack was approached. Figure 54 shows very different results across the grain boundary than the previous line. A large spike in the chromium concentration is accompanied by a corresponding decrease in the nickel intensity directly at the grain boundary. Furthermore, a small increase in both the carbon and oxygen concentration coincides with the chromium peak. Both sides directly adjacent to the grain boundary on line 2 appear to be populated by the ~ 250 nm particles which are most likely chromium carbides. This would explain both the chromium and carbon peaks. However, the increase in oxygen has not been observed on these particles before. The difference may be that the particle intersected on line 2 is directly ahead of the crack tip on the grain boundary.
Figure 53. Line scan analysis results for line 1 overlaid on the high magnification image in Figure 52 showing the intensities of chromium, nickel, oxygen, and carbon.

Figure 54. Line scan analysis results for line 2 in Figure 52.
Further line scans were conducted on the same grain boundary to possibly confirm these observations.

Six more high resolution line scans were performed on the grain boundary as shown in Figure 55. The first line is in approximately the same position as the first line in the previous analysis but slightly further away from the crack tip. The results for the six line scan are shown in Figure 56 through Figure 61. Starting with Figure 56, the results across the boundary are similar to the results from the previous two line scans in Figure 53 and Figure 54. An increase in nickel is visible directly to the right of the boundary with a corresponding drop in the chromium. Furthermore, there is a chromium and carbon peak directly on the grain boundary. Again, the oxygen concentration shows no significant changes along the whole length of the line. The remaining five line scans all exhibit similar characteristics so the discussion of these analyses will be grouped together. When each one of the lines is directly on the grain boundary, there is a clear increase in both the chromium and carbon intensity while the nickel intensity decreases. The oxygen intensity for the same regions on the boundary also show no change (e.g. Figure 60) or a small decrease (e.g. Figure 59). This is contradictory to the previous result in Figure 54 in

![Figure 55](image){width=10cm}

Figure 55. Six lines scans performed in the same region as Figure 52. Each line was placed so that it runs perpendicular to the grain boundary in the center of the picture.
that a slight increase was observed on the grain boundary. Since five of the line scans exhibited similar increases in both chromium and carbon directly on the boundary (as well as previous analyses, even for the other sample), it is reasonable to say that chromium carbides are lining the boundary. The decrease in oxygen is consistent if the line scan intersects a chromium carbide. To further discuss features of the line scan, a closer analysis of the regions directly adjacent to the boundary is needed. On a number of the lines scans, the nickel concentration shows a sharp increase in intensity on both sides of the boundary, or in other words on both sides of the chromium carbides. This increase in nickel directly adjacent to the grain boundary is most visible in Figure 60 and Figure 61. The nickel seems as though it segregates to the sides of the carbides lining the boundary or has been rejected from the precipitating carbide. The intensity of nickel obviously drops as the line passes through the carbide. This behavior has been observed before on carbides dispersed in the matrix, as in Figure 49. Furthermore, line scans on the previous sample showed similar characteristics for nickel intensities as seen in Figure 45.

Figure 56. Line scan analysis results for line 1 superimposed on the image in Figure 55 showing the intensities of chromium, nickel, carbon, and oxygen.
Figure 57. Line scan analysis results for line 2 superimposed on the image in Figure 55.

Figure 58. Line scan analysis results for line 3 superimposed on the image in Figure 55.
Figure 59. Line scan analysis results for line 4 superimposed on the image in Figure 55.

Figure 60. Line scan analysis results for line 5 superimposed on the image in Figure 55.
Figure 61. Line scan analysis results for line 6 superimposed on the image in Figure 55.
5. DISCUSSION

This section is divided into two parts. The crack growth rate results, for both fatigue and static loading, will first be discussed in detail and then comparisons to previous studies will be made. Furthermore, possible crack tip embrittlement mechanisms will be considered. The latter part of discussion will involve a detailed analysis of the Auger spectroscopy results and their relation to the observed crack growth rate results in Alloy 617.

5.1 Crack Growth Rate Data

5.1.1 Fatigue crack growth at $R = 0.1$ and $R = 0.5$

In the fatigue crack growth data with a load ratio of 0.1, which is presented in Figure 18 through Figure 21, it is important to consider the effects of frequency and oxygen potential. In terms of frequency effects, there is not enough evidence to make any conclusions about crack propagation differences between 0.1 and 2 Hz loading for either of the oxygen potentials tested. Although there appears to be a trend for the 0.1 Hz crack growth rates to be slightly higher than the 2 Hz growth rates at high oxygen potential ($P_o = 9.71 \times 10^{-4}$ atm) in Figure 19, the material tested in argon shows no such trend. As a comparison, it should be noted that the data from the test at $R = 0.5$ in argon (in which the attained oxygen potential was much lower than in the $R = 0.1$ test) even showed a distinct increase in crack growth rate for 0.1 Hz loading compared to 2 Hz loading. The most probable reasons for this result at $R = 0.1$ could include crack closure effects at the minimum peak amplitude of the sinusoidal load waveform. In terms of environmental time dependent effects, little to no change in crack growth rates would be observed at different oxygen partial pressures if this was the case. Around the minimum of the loading waveform, the crack opening may have almost completed closed due to oxide backfill and drastically hindered oxygen penetration to the crack tip. Another possibility is fresh fracture surface may have served as oxygen getters before oxygen reached the crack tip. However, Figure 20 and Figure 21 do indicate a small increase in crack growth rates with increasing oxygen potential at each 0.1 and 2.0 Hz, respectively. Previous data for Alloy 617 tested at 650°C in air noted that the fatigue crack growth is time independent below a frequency of 0.5 Hz [63], but this value is expected to change depending on the environment. Possible creep fatigue
environment interaction effects could have depressed the time dependent region to a lower frequency for the tests conducted here. Although no SEM fracture surface images were obtained for these specimens, the discussion above, along with the transgranular fracture surface obtained in Figure 30 for \( R = 0.5 \) fatigue loading but at the same exact same \( K_{\text{max}} \) values as the \( R = 0.1 \) tests, indicate that the fracture mode was mostly time independent and transgranular for these conditions. Results from fatigue in Alloy 718 in a large variety of gaseous environments even indicated that enhancement of transgranular crack growth rates due to corrosive species was possible [35]. The only time dependent process at \( R = 0.1 \) is the small effect of oxygen concentration. As noted before in contrast to the \( R = 0.1 \) growth rates, the trend found in crack growth rates at \( R = 0.5 \) shows that lower frequencies at each oxygen potential lead to slightly higher crack growth rates. This is in agreement with previous conclusions by Hsu [63] in that high \( R \)-ratios can significantly increase time dependent processes except for the contrasting detail that the crack propagation mode does not transition to intergranular. The fracture surface shown in Figure 30 indicates mostly transgranular failure for \( R = 0.5 \) and possibly a small amount of intergranular fracture.

The fatigue crack growth data with a load ratio of 0.5 under both 0.1 and 2.0 Hz loading, which was previously presented in Figure 26 and Figure 27, has been plotted versus oxygen partial pressure to clearly demonstrate the effect of oxygen. These results are shown in Figure 62 and Figure 63. Two points of discussion arise from the reorganization of the data on \( da/dN \) vs. \( P_{O_2} \) plots. The first is in relation to the existence of a transition oxygen partial pressure that is independent of the mechanical testing parameters (i.e. frequency, stress intensity factor). This transition pressure is the point at which there is an abrupt increase in crack growth rates with increasing oxygen potential and was first noted in fatigue life studies in nickel [26] and stainless steel [1] and then in fatigue crack growth rates in Alloy 718 by Molins et al. [13]. The transition pressure has also been found to vary with chromium concentration in the alloy. Although the work completed here only studied crack growth rates in Alloy 617 which contains ~22 wt. % Cr., the experiments conducted by Molins et al. included tests on the variation of the transition pressure with chromium content for binary Ni-Cr. They found that a transition pressure existed for all binary alloys tested except the Ni-30Cr alloy and also that it increased with the chromium content. For Alloy 718 with ~18 wt. % Cr, the transition pressure was approximately 0.1 Pa or \( 10^{-6} \) atm and was attributed to nucleation and growth of different oxides at low and high oxygen
partial pressure. As noted in the literature review for Alloy 718, chromium oxide formation occurred at the beginning of the oxidation process at low partial pressures whereas a NiO type oxide formed before the formation of a chromia layer at high partial pressures [14, 64]. Despite the transition pressure being independent of mechanical parameters and possibly directly linked to the oxygen embrittlement phenomenon, the amplitude and point of the transition depends on the material microstructure. The results in Figure 62 and Figure 63 indicate that the transition pressure in Alloy 617 is around $10^{-5}$ atm of oxygen and the change in crack growth rates at the transition is most likely less than an order of magnitude. The trend to have increasing crack growth rates with oxygen partial pressure and the small range in which the transition has been noted to occur in previous work ($10^1 \sim 10^2$ atm) justifies the conclusion that the Alloy 617 crack growth rates should plateau soon after the obtained data points in these two figures. In Figure 63,

![Figure 62](image)

**Figure 62.** Fatigue crack growth rates vs. oxygen partial pressure for $R = 0.5$ and 0.1 Hz loading. Note that the oxygen partial pressure range from $10^{-19} \sim 10^{-7}$ is omitted since there is no data in this region.
it should be again noted that the two data points which show a large decrease in \( \frac{da}{dN} \) for \( \Delta K = 19.2 \) and \( 22.0 \) MPa\(\sqrt{m} \) between \( 10^{-5} \) and \( 10^{-4} \) atm are presumed to be outliers (this was concluded from the trends found in fatigue loading data at \( R = 0.5 \) presented in Section 4.2.1). The divergence of Alloy 617 from the previous work on Alloy 718 is that the transition pressure for Alloy 617 is about an order of magnitude higher and the change in crack growth rates is not nearly as significant, with the increase most likely only an order of magnitude for Alloy 617 and approximately \( 10^2 - 10^3 \) m/cycle for Alloy 718. Since the main difference between these alloys is the microstructure, the embrittlement process appears to involve a combination of both local mechanical/microstructure interactions and oxidation or embrittlement processes. The \( \gamma' \) \( \text{Ni}_3(\text{Ti}, \text{Al}) \) and \( \gamma'' \) \( \text{Ni}_3\text{Nb} \) hardening precipitates and small amounts of intergranular \( \delta \)-phases (\( \text{Ni}_3\text{Nb} \)) present in Alloy 718 most likely provides the explanation in the differences between these two alloys. These hardening particles and phases can both hinder the relaxation of the crack tip stresses and also promote selective oxide formation. Since solid-solution hardened alloys such as Alloy 617 do not contain large amounts of secondary hardening phases (besides carbides), the
high temperature environmental stability and crack growth variation of Alloy 617 is minimal compared to Alloy 718, as is clearly demonstrated by the results presented here. It should be noted however that Alloy 617 does age due to precipitation but mostly at temperatures equal to or above 700°C. Intergranular formation of \( \gamma'\)-Ni\(_3\)(Al,Ti) precipitates with competitive formation of \( \delta\)-phase (Ni\(_3\)Mo) was identified after medium and long-term aging experiments at 700°C [65].

### 5.1.2 Static crack growth

The results of the static loading crack growth experiments presented in section 4.2.2 showed varying results between the two stress intensity factors tested with varying oxygen potentials. The first set of data tested at \( K = 49.5 \text{ MPa}\sqrt{\text{m}} \) indicated an increase in crack growth rates with decreasing oxygen partial pressure, as shown in Figure 28. However, it was previously noted that this portion of the test did not conform to the ASTM E647 requirements in that the specimen's uncracked ligament size requirement (i.e. specimen width - crack length) had been significantly exceeded in combination with the loads that were employed during the static loading crack growth rate measurements. For C(T) specimen, this criteria is given by Equation (1) where \( \sigma_{FS} \) is the flow stress of the material (i.e. mean of the yield stress and ultimate tensile strength).

\[
(W - a) \geq \left( \frac{4}{\pi} \frac{K_{\text{max}}}{\sigma_{FS}} \right)
\]

The flow stress is used instead of the yield strength since it accounts for material strain hardening capacity. This requirement was established so that the specimen is predominately in the elastic regime at all values of applied force. At the measured crack length during static loading of this specimen, the maximum allowable stress intensity factor would have been approximately 35.2 MPa\(\sqrt{\text{m}}\). In terms of a plastic zone size calculation, plane stress conditions yielded a plastic zone radius of approximately 3 mm meaning that a circular area approximately 6 mm in diameter was undergoing plastic deformation in the plane of loading ahead of the physical crack tip. However, this only left \( \sim 3.5 \) mm of uncracked material ligament in purely elastic loading. The result of the high stress intensity factor could have resulted in large scale plastic yielding at the crack tip, which would explain the extensive damage and crack branching on the side view of the specimen surface shown in Figure 31 and Figure 33. Furthermore, the observed effect of oxygen potential
may have had been a result of these particular static loading conditions. Knowing that there is transition time necessary to form a passive oxide scale [14], the high oxygen concentrations at which data was obtained for $K = 49.5 \text{ MPa}\sqrt{\text{m}}$, especially at $P_o \approx 10^{-3} \text{ atm}$, would have provided an ample oxygen supply to the specimen. Consequently, a passive scale such as chromium scale may have quickly formed and prevented further oxygen penetration and damage.

However, as the oxygen potential was decreased, the time necessary to form a protective oxide would increase and thus allow more oxygen ingress resulting in more extensive damage and higher crack growth rates. This, in combination with the substantial crack branching and yielding visible on the surface at these loads, may explain the resulting increase in crack growth rates with decreasing oxygen potential.

The results for static loading crack growth at $K = 45 \text{ MPa}\sqrt{\text{m}}$ contrast to the results at $K = 30 \text{ MPa}\sqrt{\text{m}}$. There was no significant change in growth rates over the entire partial pressure range tested as shown in Figure 29. Even though only three different oxygen partial pressures were able to be tested, the range of oxygen potentials covered by the test conditions should have yielded a variation in crack growth rates if an environmental effect was present. The difference in measured oxygen potentials between the argon gas and the two oxygen mixtures containing 50 and 1000 vppm $O_2$ was more than 15 orders of magnitude. Reviewing the data, the difference between the crack growth rates at these three oxygen concentrations was below 10%, which is trivial in comparison the two to three order of magnitude change in crack growth rates observed in Alloy 718 at the transition oxygen partial pressure found by Molin’s work [13]. In Figure 64, the data for the static crack growth rates vs. oxygen partial pressure are shown again. Furthermore, growth rates obtained from a trapezoidal waveform with a 250s loading, 500s hold at maximum load, and 250s unloading cycle and $\Delta K = 4.12 \text{ MPa}\sqrt{\text{m}}$ are also shown. The trapezoidal loading data still exhibits an increase in crack growth rates similar to the crack growth rate dependence on oxygen potential under fatigue loading at $R = 0.5$. However, the magnitude of the increase for the trapezoidal cycle is minor in comparison to the increase found previously in the fatigue data. The apparent trend is that oxygen damage can only occur under fatigue loading (and possible high stresses under static loading) since all of the data obtained under fatigue irrelevant of load ratio or frequency demonstrates oxygen sensitivity. As show in Figure 66 and Figure 67 in Appendix B, fatigue loading crack growth rates at higher stress ratios, $R = 0.625$ and 0.75, and lower stress intensity factor ranges, $\Delta K = 8.2$ and 12.6 MPa$\sqrt{\text{m}}$, even
show sensitivity to oxygen partial pressure similar to the fatigue loading data at R = 0.5 and also similar to the trapezoidal cycle data in Figure 64.

5.1.3 Possible crack tip damage mechanisms

In relating the above discussion of crack growth rates to the kinetics of oxygen penetration, the data compiled in Figure 65 needs to be considered. Most of the previous literature predicts that the grain boundary diffusivity of oxygen in nickel is approximately between $10^{-15}$ to $10^{-13}$ m$^2$/s. Sulfur, which is chemically similar to oxygen, has a measured intergranular diffusion coefficient of $4 \times 10^{-12}$ m$^2$/s at 700°C [66]. Furthermore, oxygen diffusion data on Ni270 from the work by lococca and Woodford can be extrapolated to 650°C and predicts diffusivities of approximately $10^{-15}$ m$^2$/s [47]. Lastly, work on IN718 at 650°C has found the intergranular diffusion coefficient to be approximately $10^{-15}$ m$^2$/s. For a simple comparison, we can assume that the oxygen diffusion depth follows the approximation for slab diffusion, $x \propto \sqrt{Dt}$. This
yields intergranular oxygen diffusion rates between $10^{-8}$ and $10^{-7}$ m/s using the above data. From the crack growth data in this work, fatigue crack growth rates were approximately $10^{-8}$ m/s for 0.1 Hz loading and $2 \times 10^{-7}$ m/s for 2 Hz loading using the lower range of the data. In terms of the oxygen penetration depth ahead of the crack tip, the similar magnitudes of the crack growth and oxygen diffusion rates indicates that any long range damage mechanisms are unlikely in the case of Alloy 617. Most of the literature discussing dynamic embrittlement argues that oxygen penetration can only occur a few nanometers (or atomic spacings) ahead of the crack tip, which appears to be supportive of the results here. Continuing the discussion of dynamic embrittlement, the question arises of why the crack growth behavior appears to be insensitive to oxygen variations when approaching static loading conditions. If dynamic embrittlement is indeed the prominent damage mechanism, then oxygen penetration and subsequent decohesion can only occur on a very short scale. The crack growth rates for both trapezoidal and static loading at $K = 33.0$ MPa$\cdot$m approaches $10^{-10}$ m/s, which is two to three orders of magnitude less than the expected intergranular oxygen diffusion rates. The difference between crack growth and oxygen diffusion rates possibly indicate that ample time was allowed for a protective oxide to form at the
crack tip. The Auger spectroscopy results did not detect any intergranular oxide formation within 1 to 2 μm ahead of the crack tip in the sensitivity of our analysis. Furthermore, the only detected oxide was in the crack wake and the results indicated that this oxide was chromium rich, which according to the literature is protective against further oxygen ingress. If the penetration depth of the oxygen was only on the order of a few atomic spacings before a protective oxide formed, the moderate stresses at the crack tip may not have been sufficient to disrupt the oxide film and enhance the crack growth rate. The dynamic embrittlement crack growth process has been known to be intermittent and can vary with local grain boundary structure. As noted before, this is due to the constraint imposed on the crack tip by regions of uncracked material along the crack front which have yet to be fractured. The constraint imposed by these uncracked regions may keep the oxide film mostly intact when there are no oscillations in the load. This could also explain why all of the fatigue loading crack growth rates increased with oxygen potential. The disruption of the protective oxide film at the crack tip, even at the low ΔK of 4.12 MPa√m used in the trapezoidal cycle, may have been sufficient to disrupt the brittle oxide and alloy the embrittlement process to repeat itself.

Lastly, the combination of the dynamic embrittlement process and protective chromium oxide formation can explain the diminishing change in magnitude of crack growth rates over the range of oxygen partial pressures when the trapezoidal loading cycle was used. The trapezoidal loading cycle was unique in that there was a 500s hold time at maximum load while the rest of the fatigue data was under continuous cycle at R = 0.5, 0.625, and 0.75. The crack growth rates from the continuous fatigue all showed similar increases in crack growth rates over the oxygen concentration range from argon gas to 1000 vppm O_2 mixtures in argon. However, the results from the trapezoidal cycle did not show as significant an increase in growth rates with increasing oxygen concentration. The hold time at maximum load may have been more similar to the static loading data where a protective oxide was allowed to form. In contrast, the segments of the trapezoidal waveform where load was being increased and decreased are more similar to the continuous sinusoidal fatigue and would have allowed the oxide to fracture slightly and oxygen to penetrate further along the boundary. Therefore, the enhancement in crack growth rates for a trapezoidal loading cycle was still detectable, unlike the static loading data, but ultimately exhibits only a minor change when compared to the continuous fatigue growth rates.
5.2 Microstructural Analysis

The results from the Auger spectroscopy have already been used in the discussions up to this point, but there are some minor details that remain. To briefly review, the microanalysis results mainly indicated that the material used in this study was heavily banded and contained extensive carbide precipitation. Chromium rich carbides were present in both the matrix and along many on the grain boundaries analyzed using line scans. Some molybdenum rich carbides were also present as shown in Figure 39. In terms of detection of intergranular oxidation, only a chromium rich oxide film was detected in the wake of cracking and not ahead of the crack tips within the resolution of our instrumentation. Even with a lateral resolution of ~10 nm, the Auger nanoprobe could only detect carbides at grain boundaries within the range of approximately 0 to 2 μm beyond the main crack tip. One of the line scans did indicate an increase in oxygen when traversing the grain boundary in Figure 54, but all of the subsequent scans did not confirm this result so no definite conclusions could be made. Therefore, the results collectively indicated that there was not extensive oxide formation prior to fracture, as was initially proposed by the SAGBO mechanism. Additionally, more recent research on crack growth in Alloy 718 has indicated that a dynamic embrittlement mechanism is more likely and only requires oxygen-induced decohesion only 1 to 2 nm ahead of the crack. This combined with further arguments in recent TEM studies detecting intergranular oxidation on the order of 10–50 nm beyond crack tips and IGSCC attack provides the most likely reason Auger spectroscopy was not able to resolve any long range oxygen diffusion. Alloy 617, which has demonstrated superior oxidation resistance to Alloy 718 under constant ΔK crack growth, possibly suffers from similar short range oxygen-induced decohesion effects as discussed in this previous literature.

One of the remaining points of discussion is that of nickel segregation at the boundary. The line scan across the visibly oxidized fracture surface in Figure 48 shows an increase in nickel intensity on each side adjacent to the oxidized fracture surface. During formation of the oxide film, chromium atoms were selectively oxidized and possibly even diffused a short distance in the near matrix material to the fracture surface causing a small zone depleted in chromium. Also, nickel solute atoms would have been rejected from the product of the oxidation reaction and built up a nickel rich zone adjacent to the oxide. Both of these statements are justified by the line scan results in Figure 49 and Figure 50. There are similarities in these observations to the line scans
which traversed grain boundaries ahead of cracks and detected intergranular chromium carbides. Both Figure 58 and Figure 60 show a depletion of chromium and an increase in nickel intensity adjacent to carbides. Since previous microstructural analysis has indicated that intergranular carbides are present in the alloy before testing, they are most likely not the result of the test environment, especially at 650°C. The enrichment of nickel adjacent to the carbides quite possibly arose during carbide precipitation at processing. These carbides, however, could very well be involved in the crack growth process if they were oxidized during crack growth and subsequently released CO during the reaction. Continuing this argument, the presence of carbides on a large percentage of the grain boundaries would have prevented long-range intergranular transport of oxygen from the environment if oxidation of carbides occurred within a few nanometers of the propagating crack. A comparison with an intergranular crack tip in a region free from intergranular carburization was needed to justify this conclusion but unfortunately a region with these characteristics was not found.
6. CONCLUSIONS

This study has examined crack growth under static and fatigue loading and varying oxygen partial pressures at 650°C. At both of the load ratios tested (R = 0.1 and 0.5), the constant ΔK fatigue data indicates that increasing oxygen potential tends to enhance crack growth rates, even during transgranular fracture. The fatigue data at R = 0.5 further indicates the presence of a transition oxygen partial pressure at \( P_{\alpha} \approx 10^{-6} \) atm at which the crack growth rates increase abruptly and is also independent of any mechanical loading parameters. The existence of a transition oxygen partial pressure has been noted previously in Alloy 718, but the Alloy 617 material tested in this work demonstrates a dramatic improvement in the resistance to oxygen induced damage during crack growth. Experiments under static loading conditions were also conducted. At a high stress intensity factor, rates were unexpectedly found to increase as the oxygen partial pressure was decreased. However, this was likely influenced by large scale yielding. At the lower stress intensity factor under static loading, the crack growth rates show no sensitivity to variations in oxygen partial pressure. Since all of the fatigue data shows an increase in growth rates with increasing oxygen partial pressure, including a trapezoidal loading cycle with 500s hold time at maximum load, disruption on an oxygen embrittled region at the crack tip appears to be necessary to cause environmentally enhanced fracture in Alloy 617.

The results here most closely relate to the dynamic embrittlement mechanism which was recently proposed for Alloy 718. This mechanism only requires surface absorption of an embrittling element such as oxygen and short range diffusion along the grain boundary (approx. 1-2 nm) which subsequently causes intergranular decohesion. Comparing the available oxygen diffusion rates for nickel and similar nickel-base alloys with fatigue crack growth rates obtained in this study, combined with the absence of long range intergranular oxidation detected by Auger spectroscopy supports the argument that oxygen damage only occurs immediately ahead of the crack tip. Furthermore, the intermittent process of crack growth observed in dynamic embrittlement studies may explain the absence of environmental sensitivity under static loading. Constraints imposed on the crack tip by regions of unfractured material along the crack front have been found to be the cause of the intermittent crack growth. In the case of static loading
crack growth, these constraints may have prevented the embrittled crack tip material from fracturing any differently under varying environmental conditions.

Finally, the Auger spectroscopy only detected a chromium rich oxide film on fracture surfaces and not on the grain boundary ahead of the crack tip. Limitations in the spatial resolution of the Augur nanoprobe most likely prevented detection of oxygen in the range likely for the proposed oxygen-induced damage. Also, trace concentrations of oxygen may not have been possible by this technique. However, the dense chromium oxide film generally protects against further oxygen ingress once the film has formed so this result is not completely unexpected. Also, due to the large amount of intergranular carbides ahead of analyzed crack tips, oxygen may have reacted with these particles before any long-range intergranular transport was allowed to occur. In summary, the argument crack growth occurs by the dynamic embrittlement process combined with observations of only chromium oxide formation (and possible reaction between oxygen and carbides) can be used to explain the trend in crack growth rates observed in this study. Although Alloy 617 is slightly susceptible to changes in environmental conditions under fatigue loading, conditions likely to exist in the intermediate heat exchanger of the VHTR will be more similar to that of the trapezoidal or static loading tests. These initial results indicate that the oxygen induced damage at 650°C do not significantly reduce the performance of the material, but more detailed studies of the crack tip using tools such as NanoSIMS, TEM/EELS, atom-probe spectroscopy, etc. are still needed to fully explain the process and intergranular damage of oxygen embrittlement.
### APPENDIX A. CRACK GROWTH RATE DATA

Table 6. Fatigue crack growth rate data with $R = 0.1$ and using a gas mixture of 1000 vppm $O_2$ in argon.

<table>
<thead>
<tr>
<th>freq.</th>
<th>R-ratio</th>
<th>$K_{max}$ (ksi(\sqrt{in}))</th>
<th>$\Delta K$ (ksi(\sqrt{in}))</th>
<th>$\Delta K$ (MPa(\sqrt{m}))</th>
<th>environment (approx.)</th>
<th>avg. partial pressure over entire step</th>
<th>crack growth rate (m/cycle)</th>
<th>crack growth rate (m/sec)</th>
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<tbody>
<tr>
<td>fatigue</td>
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<td></td>
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<td></td>
<td></td>
<td>oxygen partial pressure (atm)</td>
<td>oxygen partial pressure (Pa)</td>
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<td>0.1</td>
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Table 7. Fatigue crack growth rate data with $R = 0.1$ and $P_{O_2} < 2 \times 10^{-12}$ atm.

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<th>$\Delta K$ (MPa(\sqrt{m}))</th>
<th>environment (approx.)</th>
<th>avg. partial pressure over entire step</th>
<th>crack growth rate (m/cycle)</th>
<th>crack growth rate (m/sec)</th>
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### Table 8. Fatigue crack growth rate data with $R = 0.5$ and $P_{O_2} < 2 \times 10^{-21}$ atm.

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<th>$\Delta K$ (ksi√ln)</th>
<th>$\Delta K$ (MPa√m)</th>
<th>avg. partial pressure over entire step</th>
<th>crack growth rate (m/cycle)</th>
<th>crack growth rate (m/sec)</th>
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### Table 9. Fatigue crack growth rate data with $R = 0.5$ and using a gas mixture of 10 vppm $O_2$ in argon.

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<th>$\Delta K$ (MPa√m)</th>
<th>avg. partial pressure over entire step</th>
<th>crack growth rate (m/cycle)</th>
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Table 10. Fatigue crack growth rate data with R=0.5 and using a gas mixture of 50 vppm O_2 in argon. Also shown is the static loading crack growth rate data at K = 49.5 MPa/m with varying oxygen partial pressure used for Figure 28.

<table>
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<th>freq</th>
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<th>K (ksi/\sqrt{in})</th>
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<th>ΔK (MPa/\sqrt{m})</th>
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<td>19.23</td>
<td>argon</td>
<td>1.06535E-18</td>
<td>1.07946E-13</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.5</td>
<td>40</td>
<td>20</td>
<td>21.98</td>
<td>argon</td>
<td>2.08600E-17</td>
<td>2.11364E-12</td>
</tr>
</tbody>
</table>

Table 11. Fatigue crack growth rate data with R=0.5 and P_{O_2} < 2x10^{-17} atm.

<table>
<thead>
<tr>
<th>freq</th>
<th>R-ratio</th>
<th>K (ksi/\sqrt{in})</th>
<th>ΔK (ksi/\sqrt{in})</th>
<th>ΔK (MPa/\sqrt{m})</th>
<th>avg. partial pressure over entire step</th>
<th>oxygen partial pressure (atm)</th>
<th>oxygen partial pressure (Pa)</th>
<th>crack growth rate crack growth rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>fatigue</td>
<td>0.1</td>
<td>0.5</td>
<td>35</td>
<td>17.5</td>
<td>19.23</td>
<td>argon</td>
<td>3.64130E-19</td>
<td>3.69E-14</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td></td>
<td>35</td>
<td>17.5</td>
<td>19.23</td>
<td>argon</td>
<td>3.56748E-19</td>
<td>3.61475E-14</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.5</td>
<td>35</td>
<td>17.5</td>
<td>19.23</td>
<td>argon</td>
<td>1.06535E-18</td>
<td>1.07946E-13</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.5</td>
<td>40</td>
<td>20</td>
<td>21.98</td>
<td>argon</td>
<td>2.08600E-17</td>
<td>2.11364E-12</td>
</tr>
</tbody>
</table>
Table 12. Fatigue crack growth rate data with $R=0.5$ and using a gas mixture of 1000 vppm $O_2$ in argon.

<table>
<thead>
<tr>
<th>freq.</th>
<th>R-ratio</th>
<th>$K_{max}$ (ksi/in)</th>
<th>$\Delta K$ (ksi/in)</th>
<th>$\Delta K$ (MPa/m)</th>
<th>environment (approx.)</th>
<th>avg. partial pressure over entire step</th>
<th>crack growth rate crack growth rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>fatigue</td>
<td>2</td>
<td>0.5</td>
<td>30</td>
<td>15</td>
<td>16.48</td>
<td>1000 ppm $O_2$</td>
<td>9.477E-04</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.5</td>
<td>30</td>
<td>15</td>
<td>16.48</td>
<td>1000 ppm $O_2$</td>
<td>9.46E-04</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.5</td>
<td>35</td>
<td>17.5</td>
<td>19.23</td>
<td>1000 ppm $O_2$</td>
<td>9.44E-04</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.5</td>
<td>35</td>
<td>17.5</td>
<td>19.23</td>
<td>1000 ppm $O_2$</td>
<td>9.43E-04</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.5</td>
<td>40</td>
<td>20</td>
<td>21.98</td>
<td>1000 ppm $O_2$</td>
<td>9.47E-04</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.5</td>
<td>40</td>
<td>20</td>
<td>21.98</td>
<td>1000 ppm $O_2$</td>
<td>9.47E-04</td>
</tr>
</tbody>
</table>

Table 13. Fatigue crack growth rate data with $R=0.5$ and using a gas mixture of 1000 vppm $O_2$ in argon. Also shown is the static loading crack growth rate data at $K = 33.0$ MPa/m with varying oxygen partial pressure conditions.

<table>
<thead>
<tr>
<th>freq.</th>
<th>R-ratio</th>
<th>$K_{max}$ (ksi/in)</th>
<th>$\Delta K$ (ksi/in)</th>
<th>$\Delta K$ (MPa/m)</th>
<th>environment (approx.)</th>
<th>avg. partial pressure over entire step</th>
<th>crack growth rate crack growth rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>fatigue</td>
<td>2</td>
<td>0.5</td>
<td>30</td>
<td>15</td>
<td>16.48</td>
<td>1000 ppm $O_2$</td>
<td>9.244E-04</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.5</td>
<td>30</td>
<td>15</td>
<td>16.48</td>
<td>1000 ppm $O_2$</td>
<td>9.352E-04</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>0.625</td>
<td>30</td>
<td>11.25</td>
<td>12.36</td>
<td>1000 ppm $O_2$</td>
<td>9.409E-04</td>
</tr>
<tr>
<td></td>
<td>0.005</td>
<td>0.75</td>
<td>30</td>
<td>7.5</td>
<td>8.24</td>
<td>1000 ppm $O_2$</td>
<td>9.49E-04</td>
</tr>
<tr>
<td></td>
<td>0.002</td>
<td>0.875</td>
<td>30</td>
<td>3.75</td>
<td>4.12</td>
<td>1000 ppm $O_2$</td>
<td>9.45E-04</td>
</tr>
<tr>
<td>note: 500s hold time</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>static</th>
<th>K (ksi/in)</th>
<th>K (MPa/m)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>55µm</td>
<td>32.97</td>
<td>1000 ppm $O_2$</td>
<td>9.41E-04</td>
</tr>
<tr>
<td>90.7µm</td>
<td>32.97</td>
<td>50 ppm $O_2$</td>
<td>4.52E-05</td>
</tr>
<tr>
<td>45.8µm</td>
<td>32.97</td>
<td>50ppm $O_2$</td>
<td>4.42E-05</td>
</tr>
<tr>
<td>233µm</td>
<td>32.97</td>
<td>argon</td>
<td>1.31E-20</td>
</tr>
<tr>
<td>60.9µm</td>
<td>32.97</td>
<td>10 ppm $O_2$</td>
<td>8.53E-06</td>
</tr>
<tr>
<td>16.5µm</td>
<td>32.97</td>
<td>10 ppm $O_2$</td>
<td>9.137E-06</td>
</tr>
</tbody>
</table>
Table 14. Static loading crack growth rate data at $K = 33.0$ MPa$\cdot$m using a gas mixture of 1000 vppm O$_2$ in argon. Note that the fatigue steps documented in this table were necessary to promote crack growth under static loading.

<table>
<thead>
<tr>
<th>freq.</th>
<th>R-ratio</th>
<th>$K_{\text{max}}$ (ksi/in)</th>
<th>$\Delta K$ (ksi/in)</th>
<th>$\Delta K$ (MPa$\cdot$m)</th>
<th>avg. partial pressure over entire step (atm)</th>
<th>oxy. partial pressure (Pa)</th>
<th>crack growth rate (m/cycle)</th>
<th>crack growth rate (m/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>fatigue</td>
<td>2 0.5</td>
<td>30 15</td>
<td>16.48</td>
<td>1000ppm O$_2$</td>
<td>9.222E-04</td>
<td>93.44</td>
<td>8.442E-08</td>
<td>1.688E-07</td>
</tr>
<tr>
<td></td>
<td>0.1 0.5</td>
<td>30 15</td>
<td>16.48</td>
<td>1000ppm O$_2$</td>
<td>9.345E-04</td>
<td>94.69</td>
<td>2.456E-07</td>
<td>2.458E-08</td>
</tr>
<tr>
<td>note: 500s hold time</td>
<td>0.01 0.625</td>
<td>30 11.25</td>
<td>12.36</td>
<td>1000ppm O$_2$</td>
<td>9.326E-04</td>
<td>94.52</td>
<td>1.927E-07</td>
<td>1.927E-09</td>
</tr>
<tr>
<td></td>
<td>0.005 0.75</td>
<td>30 7.5</td>
<td>8.24</td>
<td>1000ppm O$_2$</td>
<td>9.328E-04</td>
<td>94.51</td>
<td>1.182E-07</td>
<td>5.809E-10</td>
</tr>
<tr>
<td></td>
<td>0.002 0.875</td>
<td>30 3.75</td>
<td>4.12</td>
<td>1000ppm O$_2$</td>
<td>9.23E-04</td>
<td>93.49</td>
<td>2.205E-10</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>static</th>
<th>K (ksi/in)</th>
<th>K (MPa$\cdot$m)</th>
<th>avg. partial pressure over entire step (atm)</th>
<th>oxy. partial pressure (Pa)</th>
<th>crack growth rate (m/cycle)</th>
<th>crack growth rate (m/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 μm</td>
<td>30 32.97</td>
<td>1000ppm O$_2$</td>
<td>9.26E-04</td>
<td>93.84</td>
<td>9.30E-11</td>
<td></td>
</tr>
</tbody>
</table>

Table 15. Crack growth rate data at various $\Delta K$ values for fatigue loading and static at $K = 33.0$ MPa$\cdot$m using a gas mixture of 50 vppm O$_2$ in argon.

<table>
<thead>
<tr>
<th>freq.</th>
<th>R-ratio</th>
<th>$K_{\text{max}}$ (ksi/in)</th>
<th>$\Delta K$ (ksi/in)</th>
<th>$\Delta K$ (MPa$\cdot$m)</th>
<th>avg. partial pressure over entire step (atm)</th>
<th>oxy. partial pressure (Pa)</th>
<th>crack growth rate (m/cycle)</th>
<th>crack growth rate (m/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>fatigue</td>
<td>2 0.5</td>
<td>30 15</td>
<td>16.48</td>
<td>50ppm O$_2$</td>
<td>4.333E-05</td>
<td>4.39</td>
<td>5.948E-08</td>
<td>1.190E-07</td>
</tr>
<tr>
<td></td>
<td>0.1 0.5</td>
<td>30 15</td>
<td>16.48</td>
<td>50ppm O$_2$</td>
<td>4.382E-05</td>
<td>4.44</td>
<td>1.180E-07</td>
<td>1.180E-08</td>
</tr>
<tr>
<td></td>
<td>0.01 0.625</td>
<td>30 11.25</td>
<td>12.36</td>
<td>50ppm O$_2$</td>
<td>4.57E-05</td>
<td>4.63</td>
<td>1.180E-07</td>
<td>1.180E-09</td>
</tr>
<tr>
<td></td>
<td>0.005 0.75</td>
<td>30 7.5</td>
<td>8.24</td>
<td>50ppm O$_2$</td>
<td>4.544E-05</td>
<td>4.60</td>
<td>4.579E-08</td>
<td>2.290E-10</td>
</tr>
<tr>
<td>note: 500s hold time</td>
<td>0.002 0.875</td>
<td>30 3.75</td>
<td>4.12</td>
<td>50ppm O$_2$</td>
<td>4.54E-05</td>
<td>4.60</td>
<td>2.063E-10</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>static</th>
<th>K (ksi/in)</th>
<th>K (MPa$\cdot$m)</th>
<th>avg. partial pressure over entire step (atm)</th>
<th>oxy. partial pressure (Pa)</th>
<th>crack growth rate (m/cycle)</th>
<th>crack growth rate (m/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>33.9 μm</td>
<td>30 32.97</td>
<td>50ppm O$_2$</td>
<td>4.57E-05</td>
<td>4.63</td>
<td>1.18E-10</td>
<td></td>
</tr>
<tr>
<td>73.9 μm</td>
<td>30 32.97</td>
<td>50ppm O$_2$</td>
<td>4.59E-05</td>
<td>4.65</td>
<td>6.24E-11</td>
<td></td>
</tr>
<tr>
<td>37.2 μm</td>
<td>30 32.97</td>
<td>50ppm O$_2$</td>
<td>4.72E-05</td>
<td>4.79</td>
<td>3.39E-11</td>
<td></td>
</tr>
<tr>
<td>11.7 μm</td>
<td>30 32.97</td>
<td>50ppm O$_2$</td>
<td>4.84598E-05</td>
<td>4.91</td>
<td>4.18E-11</td>
<td></td>
</tr>
</tbody>
</table>

weighted avg = 6.60552E-11
Table 16. Crack growth rate data at various ΔK values for fatigue loading and static loading at K = 33.0 MPa\text{\textsqrt{m}} and P_{o_2} < 4 \times 10^{-21} \text{ atm}.

<table>
<thead>
<tr>
<th>617-UK-11 Summary</th>
<th>avg. partial pressure over entire step</th>
<th>crack growth rate</th>
<th>crack growth rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>freq. R-ratio K_{max} (ksi\text{\textsqrt{in}}) ΔK (ksi\text{\textsqrt{in}}) ΔK (MPa\text{\textsqrt{m}}) environment (approx.) oxygen partial pressure (atm) oxygen partial pressure (Pa)</td>
<td>(m/cycle) (m/sec)</td>
<td>(m/cycle) (m/sec)</td>
<td></td>
</tr>
<tr>
<td>fatigue</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>0.01</td>
<td>0.825</td>
<td>30</td>
<td>11.25</td>
</tr>
<tr>
<td>0.005</td>
<td>0.75</td>
<td>30</td>
<td>7.5</td>
</tr>
<tr>
<td>0.002</td>
<td>0.875</td>
<td>30</td>
<td>3.75</td>
</tr>
<tr>
<td>note: 500s hold time</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>static K (ksi\text{\textsqrt{in}}) K (MPa\text{\textsqrt{m}})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>122.6 μm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>32.97</td>
<td>argon</td>
<td>4.07E-22</td>
</tr>
</tbody>
</table>
The following two plots were not reported with the other fatigue loading crack growth plots presented in Section 4.2.1 since they mainly served as intermediate steps to promote crack growth under static loading. Therefore, the crack growth rate data was achieved at intermediate stress ratios (R = 0.625 and 0.75) and also low sinusoidal loading frequencies (f = 0.01 and 0.005 Hz).

Figure 66. Crack growth rate vs. oxygen partial pressure under sinusoidal loading at $K_{\text{max}} = 33.0 \text{ MPa}\sqrt{\text{m}}$, $f = 0.01$ and $R = 0.625$. 
Figure 67. Crack growth rate vs. oxygen partial pressure under sinusoidal loading at $K_{\text{eff}} = 33.0$ MPa$\sqrt{\text{m}}$, $f = 0.005$ and $R = 0.75$. 
APPENDIX C. DCPD CRACK GROWTH MEASUREMENT

The following information regarding the DCPD measurement technique utilized in this research was exchanged between Peter L. Andresen (GE Global Research Center) and Pete Stahle (MIT). The personal communication briefly describes how the closed form DCPD equations were developed and additionally describes the procedure for specimen setup to correctly employ the closed form fit. Table 17 presents the finite element calculations used to calculate the curve fit equation.

GE Crack Growth DCPD Method

Pete,

Here is the closed form fit I've worked out. We're actually not using these, but it's from sloth. They are *very, very, very* close to the polynomials we use, whose disadvantage is that you can effectively not compute a closed form reversed solution for a polynomial (there are web sites that will do this, but the resulting solution takes about 5 sq. miles of paper to print out for a 5th order poly).

This should be self-explanatory. In my software (and my head), I keep two independent "potential scales" -- one is the real data, one is the conceptual (fitted) data. So when I start a test, I use the reverse fit to calc a (conceptual) potential from a known (as-machined) crack length. In turn, at the start of the test, I equilibrate the chemistry and load (typically ~80% of test load) and measure initial dcpd values. Both are "initial potentials" and I scale them proportionately. So if the measured dcpd goes up the 1%, I calculate 1.01 * the "conceptual potential", then enter that new value into the normal fit (potential >> a/W). I suspect you know this stuff.

The fits use current probes placed at the center of the top and bottom, 9.5 mm from the back face.
Table 17. Peter L. Andresen's closed form fit DCPD equation developed from finite element analysis.

**PL Andresen Closed Form dcpd Equations**

<table>
<thead>
<tr>
<th>FE calcs taken from Q18:R38 above</th>
<th>a/W-calcs</th>
<th>a/W-data</th>
<th>Pot-data</th>
<th>Pot-calc</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3000</td>
<td>0.3</td>
<td>0.82888</td>
<td>0.824109</td>
<td></td>
</tr>
<tr>
<td>0.3250</td>
<td>0.325</td>
<td>0.87615</td>
<td>0.879987</td>
<td></td>
</tr>
<tr>
<td>0.3500</td>
<td>0.35</td>
<td>0.93496</td>
<td>0.939963</td>
<td></td>
</tr>
<tr>
<td>0.3750</td>
<td>0.375</td>
<td>1</td>
<td>1.004378</td>
<td></td>
</tr>
<tr>
<td>0.4000</td>
<td>0.4</td>
<td>1.0708</td>
<td>1.073613</td>
<td></td>
</tr>
<tr>
<td>0.4250</td>
<td>0.425</td>
<td>1.1487</td>
<td>1.148085</td>
<td></td>
</tr>
<tr>
<td>0.4500</td>
<td>0.45</td>
<td>1.2286</td>
<td>1.22826</td>
<td></td>
</tr>
<tr>
<td>0.4750</td>
<td>0.475</td>
<td>1.3165</td>
<td>1.314652</td>
<td></td>
</tr>
<tr>
<td>0.5000</td>
<td>0.5</td>
<td>1.4109</td>
<td>1.407834</td>
<td></td>
</tr>
<tr>
<td>0.5250</td>
<td>0.525</td>
<td>1.5124</td>
<td>1.508446</td>
<td></td>
</tr>
<tr>
<td>0.5500</td>
<td>0.55</td>
<td>1.6215</td>
<td>1.617204</td>
<td></td>
</tr>
<tr>
<td>0.5750</td>
<td>0.575</td>
<td>1.739</td>
<td>1.734911</td>
<td></td>
</tr>
<tr>
<td>0.6000</td>
<td>0.6</td>
<td>1.8658</td>
<td>1.862475</td>
<td></td>
</tr>
<tr>
<td>0.6250</td>
<td>0.625</td>
<td>2.0029</td>
<td>2.00092</td>
<td></td>
</tr>
<tr>
<td>0.6500</td>
<td>0.65</td>
<td>2.1515</td>
<td>2.15141</td>
<td></td>
</tr>
<tr>
<td>0.6750</td>
<td>0.675</td>
<td>2.3133</td>
<td>2.315272</td>
<td></td>
</tr>
<tr>
<td>0.7000</td>
<td>0.7</td>
<td>2.4899</td>
<td>2.494025</td>
<td></td>
</tr>
<tr>
<td>0.7250</td>
<td>0.725</td>
<td>2.6839</td>
<td>2.689417</td>
<td></td>
</tr>
<tr>
<td>0.7500</td>
<td>0.75</td>
<td>2.8982</td>
<td>2.90347</td>
<td></td>
</tr>
<tr>
<td>0.7750</td>
<td>0.775</td>
<td>3.1368</td>
<td>3.138535</td>
<td></td>
</tr>
<tr>
<td>0.8000</td>
<td>0.8</td>
<td>3.4051</td>
<td>3.397362</td>
<td></td>
</tr>
</tbody>
</table>

Dec'03 effort to find curve fit eqn with closed form, mathematic inverse
Use CurveFit 1.3 with Iterations=1000

Reverse Fit:

Logistic Model: \( y = \frac{a}{1 + b \exp(-cx)} \)

Coefficient Data:

- \( a = -10.7615 \)
- \( b = -29.15836 \)
- \( c = 2.43175 \)

Standard Error: 0.0041727
Correlation Coefficient: 0.9999872
REFERENCES


