**STRESS ACCELERATED GRAIN BOUNDARY OXIDATION OF INCOLOY
ALLOY 908 IN HIGH TEMPERATURE OXYGENOUS ATMOSPHERES**

by

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**Submitted to the Department of Materials Science and Engineering
in Partial Fulfillment of the Requirements
for the Degree of**

Doctor of Science in Metallurgy

at the

Massachusetts Institute of Technology

June 1995

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ABSTRACT

Constant load stress rupture tests were performed on alloy 908. The test matrix used varied oxygen concentration, applied load, temperature, and percent cold work. The effect of modifying surface residual stresses on intergranular oxidation and cracking was examined using constant strain C-ring tests.

The mechanism for high temperature intergranular fracture in alloy 908 is stress assisted intergranular oxidation cracking. A direct correlation between percent intergranular fracture and oxygen concentration was observed. This result was comparable to the oxidation assisted, intergranular fracture behavior of alloy 718. Internal oxidation, for temperatures at or near 650°C and under an applied tensile stress, manifests itself as intergranular oxidation in alloy 908. Intergranular oxidation penetrates to the same depth as predicted for internal oxidation. The concentration of Cr incorporated into the intergranular oxide increases with increasing test duration. This result is consistent with internal oxidation theory. The depth of intergranular oxidation is controlled by both the oxygen partial pressure and the Cr concentration of the alloy. These factors influence the growth of intergranular Cr_2O_3 and NiCr_2O_4 precipitates that serve to block the diffusion path for oxygen. Analogous to internal (matrix) oxidation, a transition from intergranular to external oxidation in alloy 908 occurs when the partial pressure of oxygen at the surface is below 7.6×10^{-4} Torr.

The activation energy for intergranular oxidation in air was determined to be 202 kJ/mole for this alloy. At low (< 195 ppm) oxygen concentrations, the activation energy for intergranular oxidation increased to 500 kJ/mole. This higher value reflects the oxygen concentration dependence observed for intergranular oxidation. The dependence on alloy Cr concentration is similar to that observed for intergranular stress corrosion cracking in aqueous environments.

An oxygen concentration threshold based on zero percent intergranular fracture is a better indicator of the potential for intergranular fracture during heat treatment than one based on time to rupture. An oxygen partial pressure below 1×10^{-4} Torr is recommended for heat treatment of alloy 908 under residual or applied stresses. Shot peening appears to be a relatively simple solution to the stress accelerated grain boundary oxidation problem.

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TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
I. INTRODUCTION	15
A. Low Coefficient of Thermal Expansion Nickel-Iron Base Superalloys	15
B. Cable-In-Conduit-Conductor Nb ₃ Sn Magnets	17
C. Stress Accelerated Grain Boundary Oxidation	19
D. Remedies For Stress Accelerated Grain Boundary Oxidation	19
E. Microstructural Characteristics of Low Coefficient of Thermal Expansion Nickel-Iron Base Superalloys	20
F. Stress Accelerated Grain Boundary Oxidation and Alloy 908	21
II. LITERATURE REVIEW	23
A. Fatigue Crack Growth Rate in Air Versus Vacuum	24
B. Tensile Embrittlement and Stress Rupture Life	25
C. Role of Microstructure and Alloy Chemistry	30
D. The Effect of Oxygen Partial Pressure	31
E. Effects of Oxygen Partial Pressure and Stress on Intergranular Oxidation	32
F. Intergranular Oxidation	36
G. Application to Stress Accelerated Grain Boundary Oxidation in Alloy 908	41
III. PROCEDURES	43
A. Material	43
B. Stress Rupture Test Procedure	44
C. C-Ring Residual Stress Modification Study	50
IV. RESULTS	53
A. Microhardness and Grain Size	53

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
IV. RESULTS	53
B. Stress Rupture Results	56
C. Effect of Oxygen Concentration	61
D. Interrupted Flat Plate Tests, Microstructure and Chemistry	76
E. Round Bar Microstructure and Fractography	93
F. Grain Boundary Analysis	98
G. Modification of Residual Stresses in C-Ring Test Samples	118
V. DISCUSSION	135
A. Stress Rupture Results	135
B. Grain Boundary Analysis	148
C. C-Ring Tests and Modification of Residual Stresses	156
F. Analysis of Stress Accelerated Grain Boundary Oxidation	159
VI. SUMMARY	170
VII. CONCLUSIONS	173
VIII. FUTURE WORK	175
APPENDIX	176
REFERENCES	181

LIST OF FIGURES

<u>Figure</u>	<u>Description</u>	<u>Page</u>
1	Mean coefficient of expansion, from room temperature to temperature shown, of alloy 903 for four levels of Cr.	16
2	Crack growth rate in air as a function of temperature at, showing the change in micromechanism of crack growth with changes in frequency.	26
3	Variation in fatigue crack growth rate with test frequency and temperature for alloy 718 at 550 and 650°C.	26
4	Effect of a hold time applied at zero load on the fatigue crack growth rate ratio $(da/dN_{hold})/(da/dN)$.	27
5	Schematic comparison of stress accelerated grain boundary oxidation cracking mechanism proposed by McMahon and Coffin and that proposed by Bricknell and Woodford.	29
6	Fatigue crack growth rate as a function of the oxygen partial pressure under constant ΔK at 650°C in alloy 718.	34
7	Percent intergranular fracture in alloy 718 slow strain rate test (8.3×10^{-4} mm/s) at 650°C versus oxygen partial pressure.	34
8	Results of oxide identification by Auger spectroscopy on electropolished specimens of alloy 718, showing transition time, t_p , between both forms of oxides as a function of oxygen partial pressure.	35
9	Influence of residual stresses on the transition in oxidation mechanism. Cr-rich oxide is preferentially formed on shot peened specimens of alloy 718 at 650°C.	35
10	Lateral growth of Cr_2O_3 layer originating from grain boundaries.	37
11	Intergranular oxide formation beneath a Cr_2O_3 surface scale.	38
12	Transition from internal to external oxidation for Ag-In alloys at 550°C.	40
13	Double edge notch stress rupture specimen, $K_t = 4.5$.	46
14	Double notch round bar stress rupture specimen $K_t = 4.1$.	47
15	Illustration showing of arrangement furnace, retort, and gas analyzers used for alloy 908 stress rupture tests.	49
16	C-ring specimen holder designed to maintain a constant plastic strain of 6% during heat treatment.	52

LIST OF FIGURES

<u>Figure</u>	<u>Description</u>	<u>Page</u>
17	(a) Grain size and orientation of 3.43 mm thick sheet starting material, heat Y9401K, used for the flat plate stress rupture test samples. (b) Grain size in stress rupture tested sample 61P (650°C/118 hours).	54
18	(a),(b) Optical micrographs showing grain size in the flat plate sample 49P and round bar sample 1B, respectively. (c), optical micrograph of elongated grain in 20% cold worked material, heat Y9210, (d) SEM micrograph of the same area as in (c) after 650°C/200h vacuum heat treatment.	55
19	650°C HVN of all stress rupture test samples compared with the aging curves for solution annealed (980°C/1h) and 20% cold work starting conditions.	57
20	Comparison of 650°C flat plate test sample stress rupture data for alloy 908 in argon with controlled oxygen concentration and the same heat treat of material but with 5% cold work and tested in air.	58
21	Distribution of times to failure versus oxygen concentration for flat plate samples tested at 650°C and in the stress range 651.5 ± 18 MPa.	59
22	Effect of temperature on time to rupture versus stress for solution annealed flat plate samples at 750, 700 and 550°C for different ranges of oxygen concentration.	60
23	Comparison of 20% cold work double notch round bar air data with low oxygen concentration test data for the same heat of material with 20% cold work, 10% cold work, and solution annealed starting conditions.	62
24	Comparison of time to rupture versus stress for vacuum (1×10^{-5} torr) heat treated (650°C / 200 hours) then tested samples with samples tested in their as received condition.	63
25	Micrographs of 650°C sample 9P (640 MPa, 82.3h, 6 ppm O ₂). (a,b) Stereomicrographs of reconstructed specimen after failure showing deformation pattern in region of notch. (c) Optical micrograph of cross-section.	64
26	550°C sample 30P loaded at 644 MPa in 1.2 ppm O ₂ . Test stopped after 478.3 hours. (a,b) SEM micrographs showing exterior of sample at notch section. (c) Optical micrograph showing cross section of unfailed notch.	65
27	Characteristics of flat plate stress rupture fracture surfaces as a function of oxygen concentration.	67

LIST OF FIGURES

<u>Figure</u>	<u>Description</u>	<u>Page</u>
28	HVN from microhardness trace along the longitudinal axis (tensile) of the stress rupture sample 5P (650°C, 652 MPa, 44.1 hours, 53 ppm oxygen). Trace extends, in cross section, from the rupture surface down the center of the sample on the LT plane.	68
29	HVN from microhardness trace along the transverse axis (notch to notch) of the stress rupture sample 5P (650°C, 652 Mpa, 44.1 hours, 53 ppm oxygen).	69
30	SEM micrographs comparing the intergranular fracture morphology in 650°C/650MPa samples as a function of oxygen concentration. (a) 31P, 71.7h to failure, 1 ppm O ₂ , (b) 9P, 82.3h to failure, 6 ppm O ₂ , (c) 62P, 122h to failure, 38 ppm O ₂ , (d) 24P, 111.4h to failure, 1000 ppm O ₂ .	71
31	(a-c) Optical micrographs of notch fractures and (d-f) SEM micrographs of fracture surfaces for three 650°C samples	72
32	Fully ductile fracture shown in (a) with creep voids present in cross section, grain deformation at notch. (b) Intergranular ledge at notch with no grain deformation visible in this zone, ductile zone after intergranular ledge shows grain deformation.	73
33	SEM micrographs showing the effect of temperature on fracture for a stress of 650 MPa and 195 ppm O ₂ .	74
34	Percent intergranular fracture versus oxygen concentration for 650°C and 651±18 MPa stress range flat plate test samples.	75
35	Ratio of ductile fracture area to total fracture area versus oxygen concentration for flat plate samples at 650°C and 651.5 ± 18 MPa stress range.	77
36	Percent intergranular fracture versus oxygen concentration for all samples, flat plate and round bar, tested at 650°C and for all stress levels tested, range 535 ± 140 MPa.	78
37	Comparison of 650°C Inconel 718 slow strain rate (8.3x10 ⁻⁴ mm/s) tensile data with 650°C notched stress rupture data from alloy 908 at 649 ± 18 MPa stress range.	79
38	Micrographs comparing the notch morphologies of the 650°C/540MPa samples.	80
39	Energy dispersive spectroscopy composition profile of Fe, O, Ni, and Cr from the surface of the notch of sample 8P obtained by SEM at 12,000x magnification.	81

LIST OF FIGURES

<u>Figure</u>	<u>Description</u>	<u>Page</u>
40	Energy dispersive spectroscopy composition profile of Fe, Ni, Nb, Ti, Al, and Si from the surface of the notch of sample obtained by SEM at 4000x magnification.	82
41	Flate plate 650°C sample 38P, test stopped at 522 hours. (a) Grain boundary microstructure at base of notch after test. (b) Higher magnification of region analyzed by x-ray mapping.	84
42	Energy dispersive spectroscopy composition profile of Fe, O, Ni, and Cr from the surface of the notch of sample 38P.	85
43	Energy dispersive spectroscopy composition profile of Fe, Ni, Ti, Nb and Al from the surface of the notch of sample 38P.	86
44	EDS x-ray map of grain boundaries at base of notch in 650°C sample 38P.	87
45	(a), (b), (c) SEM micrographs and (d) optical cross-section of notch from 650°C sample 60P.	89
46	(a), (b) SEM micrographs from 650°C sample 60P showing intergranular/ ductile transgranular fracture transition.	90
47	SEM micrographs (a-d) from 650°C sample 60P.	91
48	(a,d) Optical micrographs of notch cross-sections and (b,c,e,f) SEM micrographs of 650°C samples 31P and 32P.	92
49	20% cold-worked 650°C round bar test sample 20cw31. (a) Grain structure showing large, elongated grains parallel to the rolling and tensile directions. (b) Cross-section near unfailed notch showing elongated grain at the notch and crack path. (c) Detail of crack path around elongated grain at notch.	94
50	SEM micrograph showing the fracture surface of the failed notch from the 650°C round bar sample 20cw31.	95
51	SEM micrograph of the failed notch in the 650°C round bar sample 1A.	96
52	(a) Normarski optical micrograph of the crack path at the unfailed notch in the 650°C round bar sample 10cw2. (b) SEM micrograph from a portion of an oxidized crack path extending from the unfailed notch in the 650°C round bar sample.	97
53	(a) Line scan profiles of elements across two grain boundaries in the 650°C sample 1B. (b) Enhanced oxygen line scan. (c) Area used for line scan across two grain boundaries.	99

LIST OF FIGURES

<u>Figure</u>	<u>Description</u>	<u>Page</u>
54	EDS maps of the elements present at grain boundaries near root of notch in 650°C round bar sample 1B.	100
55	(a) SEM micrograph and (b) oxygen x-ray map of grain boundaries in 650°C sample 10cw.	102
56	EDS X-ray map of elements present along grain boundaries at the unfailed notch of sample 10cw-2.	103
57	Affected grain boundaries in 650°C sample 1B. (a) General region. (b) Grain boundary at triple point selected for EDS composition profile.	104
58	EDS composition profile across a grain boundary in the 650°C round bar sample 1B.	105
59	EDS composition profile across a grain boundary in the 650°C round bar sample 1A.	106
60	EDS composition profile across an affect grain boundary in the 650°C round bar sample 1A.	108
61	(a) SEM micrographs of oxidized grain boundaries in 650°C flat plate sample 62P. (b) Micrograph of grain boundary selected for compositional analysis by EDS.	109
62	EDS composition profile along grain boundary extending to terminus. 650°C flat plate sample 62P.	110
63	EDS composition profile across grain boundary in the 650°C flat plate sample 62P.	111
64	SEM micrographs of 650°C flat plate sample. (a) Affected grain boundary extending in from failed notch. (b) Grain boundary used for compositional analysis.	112
65	EDS composition profile along grain boundary in the 650°C flat plate sample 49P.	113
66	EDS composition profile across grain boundary in the 650°C flat plate sample 49P).	114
67	(a) SEM micrograph of crack at notch in round bar sample 20cw-24 (b) SEM micrograph of grain boundary at the farthest distance from notch used for compositional analysis.	115
68	EDS composition profile along grain boundary in the 650°C round bar sample 20cw24.	116

LIST OF FIGURES

<u>Figure</u>	<u>Description</u>	<u>Page</u>
69	(a) Macrophoto of cracked C-ring S37. (b) SEM micrograph showing intergranular through crack in C-ring.	119
70	(a) Stereomicrograph showing dimpled surface of C-ring surface after shot peening. (b) SEM micrograph of shot peened surface at bend in C-ring S13.	120
71	(a-d) Optical micrographs showing cross sections of the outer surfaces of C-ring test samples heat treated at 650°C for 24 hours in a 4×10^{-2} Torr vacuum.	122
72	Microhardness profile across thickness of C-ring sample S13.	123
73	Microhardness profile across thickness of C-ring sample S49.	124
74	Microhardness profile across thickness of C-ring sample S37.	125
75	Compositions of oxides (oxygen excluded from plot) electrolytically extracted from the surfaces of C-rings that were heat treated under degraded vacuum conditions (10^{-2} Torr range).	126
76	SEM micrograph across intergranular crack in the C-ring S37.	128
77	High magnification SEM micrographs taken near the inside diameter of the cracked cross section of C-ring S37.	129
78	High magnification SEM micrographs taken along the cracked cross section of C-ring S37 after failing within 24 hours at 650°C in a 4×10^{-2} Torr vacuum.	131
79	High magnification SEM micrographs of the intergranular fracture surface from a cross section of the C-ring C33.	132
80	(a) SEM micrograph taken from the intergranular fracture surface from a cross section of the C-ring C33. (b) Oxide particles captured on an extraction replica of the C-ring fracture surface. (c) Comparable SEM micrograph from the flat plate stress rupture sample 49P.	133
81	Larson-Miller parameter plot for all flat plate test data, grouped by oxygen concentration with $C = 20$.	137
82	Larson-Miller parameter plot of low oxygen concentration flat plate test data compared with 5% cold work flat plate test data.	139
83	Larson-Miller parameter plot of round bar low oxygen concentration data for 20% cold work and solution annealed conditions compared with round bar data for 20% cold work material in air.	140

LIST OF FIGURES

<u>Figure</u>	<u>Description</u>	<u>Page</u>
84	Larson-Miller parameter plot of combined round bar and flat plate test data.	141
85	Larson-Miller parameter plot of flat plate test data at low oxygen concentrations grouped by percent intergranular fracture.	143
86	Plot of isostress lines and least squares fits for 650 and 540 MPa stresses.	145
87	Plot of isostress lines and least squares fit for 650 and 540 MPa stresses.	146
88	“Master curve” for solution annealed flat plate stress rupture data based on new material constant $C = 30$.	147
89	Arrhenius activation energy, Q_{gb} plot for intergranular oxidation in alloy 908 in air.	153
90	Arrhenius activation energy, Q_{gb} plot for intergranular oxidation in alloy 908 in 195 ppm oxygen.	154
91	Arrhenius activation energy, Q_{gb} plot for intergranular oxidation in alloy 908 in 38-195 ppm oxygen.	155
92	Arrhenius activation energy, Q_{gb} plot for intergranular oxidation in alloy 908 in 6-1000 ppm oxygen. Based on flat plate stress rupture data.	157
93	Concentration profile for the exclusive internal oxidation of alloys.	162
94	SEM micrograph showing cross section through the oxidized surface of heat treated alloy 905.	162
95	Comparison of experimental and calculated intergranular oxidation depths.	164
96	Calculated time to reach depth of intergranular oxidation observed in stress rupture tests at 650°C and 650 Mpa.	166
97	Intergranular oxidation zone (of depth ξ) developed under tensile loading.	167
98	Time to develop a 0.5 mm deep zone of internal oxidation in three alloys at 650°C as a function of oxygen concentration and mole fraction Cr.	168

LIST OF FIGURES

<u>Figure</u>	<u>Description</u>	<u>Page</u>
99	Percent intergranular fracture as a function of grain boundary Cr level in Ni-Cr-Fe alloys obtained from constant extension rate tests at room temperature.	169

LIST OF TABLES

<u>Table</u>	<u>Description</u>	<u>Page</u>
1	Compositions of the 9XX-Type LCIN Superalloys.	17
2	Chromium Concentration In Dilute Ni-Cr Alloys at the Advancing Front of Internal Oxidation.	39
3	Compositions of Alloy 908 Used for Stress Rupture Testing.	44
4	Test Matrix Used For Stress Rupture Tests.	45
5	Alloy 908 C-Ring Test Results at 650°C, 6% Plastic Strain.	118
6	Compositions of Surface and Grain Boundary Oxides From Alloy 908 Stress Rupture Samples.	149
1A	Nominal Compositions of Some Superalloys	176
2A	Alloy 908 Stress Rupture Data I.	177-178
3A	Alloy 908 Stress Rupture Data II.	179-180

ACKNOWLEDGMENT

This thesis is dedicated to the memory of

Ralph Hamilton Marler, Jr.

I. INTRODUCTION

Alloy 908 was developed as a Nb₃Sn Cable-In-Conduit-Conductor (CICC) magnet sheathing material. [1] It can be characterized as a low coefficient of thermal expansion iron-nickel base superalloy that contains 4 weight percent chromium. Its chemistry, microstructure and mechanical properties have been optimized for Cable-In-Conduit-Conductor use while maintaining a coefficient of expansion that is compatible with this application. The development of alloy 908 centered on three areas that were necessary for its successful application as a low coefficient of expansion cryogenic structural material. These were; its mechanical properties at cryogenic temperatures, welding, and its susceptibility to intergranular oxygen embrittlement. The latter of these is the area with which this thesis will deal. The application, development, and properties have been reported in other publications, so these will be mentioned here only briefly or when applicable. [1, 2, 3]

A. Low Coefficient of Thermal Expansion Iron-Nickel Base Superalloys

The low coefficient of thermal expansion iron-nickel base (LCIN) superalloys form a subset of the general class of multicomponent face centered cubic (fcc), ferromagnetic, Ni-Fe base superalloys. The thermal expansion of a low coefficient of thermal expansion iron-nickel base superalloy, however, does not exhibit a continuous increase with increasing temperature. [4,5] Although the compositions of alloys in this group have been modified to provide high temperature strength, all are derivatives of a binary Ni-Fe alloy called Invar. The Invar designation corresponds to an alloy whose composition (36 at.% Ni-Fe) produces the minimum value of coefficient of expansion (α). [5, 6] Since the thermal expansion anomaly always occurs in the vicinity of the Curie point, where the magnetic transformation from ferromagnetic to paramagnetic occurs, most theories assume that the origin of the low α is associated with the ferromagnetism of Invar alloys. [5, 6, 7] This effect is thought to be related to a decrease in the normal thermal expansion of the lattice by volume magnetostriction. [5] This produces the anomalously low mean coefficient of thermal expansion, (α_m), of these alloys. [4, 7, 8, 9] In practical terms, if (α_m) of these alloys is measured over an extended temperature range, starting at 4K and with increasing temperature α_m will appear to be constant until the inflection temperature, (T_i), is reached, after which it begins to increase.

The applications for which low coefficient of thermal expansion iron-nickel base superalloys were designed, include close tolerance components such as seals in gas turbine engines that require a constant α_m over the temperature range from 25°C to 650°C. [10]

Other than the matrix balance of Ni, Fe and Co, the primary compositional change that distinguishes these alloys from conventional superalloys is their low chromium content. This is due to the strong effect of Cr in lowering the Curie temperature, and hence the onset of volume magnetostriction. The effect of increasing Cr on α_m is shown in Figure 1. A typical low coefficient of thermal expansion iron-nickel base superalloy contains less than 1 weight percent Cr to maintain a constant α_m from 25 to 650°C. [4, 10] The base Ni-Fe chemistries are adjusted to compensate for the loss of Ni to the strengthening precipitate during precipitation hardening heat treatments. This results in the Ni content of the γ phase, after precipitation hardening, approximating that of an Invar-type alloy. [4, 11] Table 1 lists the compositions of some of the 9XX-type low coefficient of thermal expansion iron-nickel base superalloys.

Figure 1. Mean coefficient of expansion, from room temperature to temperature shown, of alloy 903 for four different levels of Cr. [1]

Table 1. Compositions of the 9XX-Type Low Coefficient of Thermal Expansion Iron-Nickel Base Superalloys

Alloy	Composition (weight percent)											
	Fe	Cr	Ni	Co	Nb	Ti	Al	Mo	Mn	C	Si	Ti + Al* Nb
903	40.9	—	38.0	15.0	3.00	1.40	0.90	0.50	0.20	0.03	—	1.89
903A	41.8	—	37.5	14.0	5.00	1.60	0.02	—	—	0.01	—	0.63
905	44.4	—	48.9	0.33	4.70	1.59	0.04	—	0.05	0.01	—	0.68
907	42.3	—	38.4	13.0	4.70	1.50	0.03	—	—		0.10	0.64
908	40.8	4.12	48.7	—	3.04	1.54	1.10	—	0.09	0.01	0.17	2.22
909	40.7	—	38.2	16.0	3.00	1.75	1.00	—	—	0.03	0.40	0.64
* Based on atomic %												

B. Cable-In-Conduit-Conductor Nb₃Sn magnets

The most recent use for one member of the general class of 9XX-type low coefficient of thermal expansion iron-nickel base superalloys, alloy 908, is in the non-conventional application as a structural alloy in advanced high magnetic field Nb₃Sn superconductor magnets. [12, 13, 14, 15] The "Cable-In-Conduit-Conductor" is an example of this magnet type. In this application, the low α_m superalloy is incorporated as a conduit that houses the brittle Nb₃Sn superconductor to provide both structural support and a coolant channel through which liquid He at 4.2K will flow.

Along with the requirement of a low Cr content, a low coefficient of thermal expansion iron-nickel base superalloy, when used in Cable-In-Conduit-Conductor applications, must not contain cobalt. This is an important consideration since cobalt has a high activation cross section in the presence of a neutron flux and one potential application for Cable-In-Conduit-Conductor magnets is in neutron producing fusion reactors.

It was first proposed by Steeves, et al., that the low thermal expansion characteristics of the 9XX series of alloys could be used to advantage in Cable-In-Conduit-Conductor applications. [16, 17] The low α_m 's and precipitation hardening characteristics of these alloys act in unison both to reduce the amount of thermal strain imposed on the conductor and to provide mechanical support for the superconductor, respectively. The strain sensitivity of Nb₃Sn, coupled with thermal strain induced lowering of critical current

density, is the single most important factor in selecting a low coefficient of thermal expansion iron-nickel base superalloy for the Cable-In-Conduit-Conductor application. [18, 19] The source of thermal strain stems from the contraction of the conduit material when the Cable-In-Conduit-Conductor structure is cooled from heat treatment temperature down to an operating temperature of 4.2K. [16, 17, 19, 20] In the specific Cable-In-Conduit-Conductor application for which the 9XX series of alloys were evaluated, the conduit alloy must remain microstructurally stable during an Nb₃Sn heat treatment cycle. For this application, a stable microstructure is one in which the precipitation hardening phase(s) will not coarsen to the extent that the 4.2 K yield strength falls below 1200 MPa, nor should the elongation be reduced by intergranular or interdendritic fracture due to the formation of embrittling phase(s), and the fracture toughness should be at or above 200 MPa√m. [1, 21] These criteria, however, must be met using heat treatments designed to optimize the solid state reactions necessary for the formation of superconducting Nb₃Sn from elemental Nb and Sn. [22] The elemental precursors for this reaction are present in a cabled "composite" wire that can either be composed of filamentary Nb surrounding Sn cores in a Cu matrix, or filamentary Nb in a Sn-Cu bronze matrix. [23] As will be discussed below, heat treatments designed to optimize Nb₃Sn formation are not optimal for most structural materials.

One processing scheme that has been successful utilizes a tube mill. The cabled wire is fed onto a strip of annealed alloy that is then formed around the cable and closed by autogenous inert gas tungsten-arc (GTA) welding. [12, 13, 24] After welding, the conduit undergoes a reduction in cross-section in the tube mill. Finally, the magnet is given a sequential heat treatment that extends over a temperature range starting at 375°C up to a possible maximum of 750°C. The typical heat treatment practice used with Cable-In-Conduit-Conductor magnets involves the continuous flow of gettered helium through the internal void space in the conduit/cable composite and an exterior vacuum greater than 1×10^{-4} Torr. [14, 15]

Heat treatment practice used for the magnet structure places two important constraints on the structural alloy. The first of these is that, since Nb₃Sn conductors, and therefore heat treatments, are constantly evolving, it is imperative that the conduit alloy's precipitation hardening window be flexible enough to overlap that of the conductor being used. In addition, resistance to environmental embrittlement and cracking in a variety of furnace atmospheres must be considered. Early tests showed that most of the then-available low coefficient of thermal expansion iron-nickel base superalloys were found to be deficient in one of these areas. [25, 26, 27] This was to be expected, since the original

processing, time, and temperature envelopes for most of these alloys were developed around optimizing properties for gas turbine applications. These envelopes do not overlap well with those that are optimal for Nb₃Sn formation, nor with the unique processing scheme developed for the Cable-In-Conduit-Conductor magnets. As a result, the Nb-Sn conductor heat treatments often produce an overaged microstructure with reduced mechanical properties compared with those of the peak age hardened condition. [26 , 27]

C. Stress Accelerated Grain Boundary Oxidation

A long recognized limitation in the use and fabrication of low coefficient of thermal expansion iron-nickel base superalloys is their susceptibility to environmentally induced intergranular cracking. [28, 29, 30] The particular form of environmentally induced cracking to which these alloys are susceptible is termed stress accelerated grain boundary oxidation (SAGBO). The term “stress accelerated grain boundary oxidation” originated with the work of McMahon and Coffin. [31] As the name indicates, it is a synergistic effect of residual (plastic) stress or imposed stress, temperature, and the presence of oxygen. Examination of fracture surfaces produced by stress accelerated grain boundary oxidation show severe intergranular cracking accompanied by substantial intergranular oxide formation. [25] Stress accelerated grain boundary oxidation cracking is a subclass of the general environmental degradation phenomena termed stress corrosion cracking (SCC). Mechanisms proposed for stress accelerated grain boundary oxidation will be discussed in the Literature Review.

Some of the general characteristics of stress accelerated grain boundary oxidation in low coefficient of thermal expansion iron-nickel base superalloys are preferential oxide formation along grain boundaries, decreased stress-rupture life in the 550°C to 800°C temperature range in air, and intergranular cracking at notch sections of stress-rupture specimens or in bend sections of U-bend samples. High temperature (> 900°C) air exposure of unstressed low coefficient of thermal expansion iron-nickel base superalloys produces varying depths of internal oxidation along with preferential oxidation of grain boundaries within the internally oxidized region.

D. Remedies For Stress Accelerated Grain Boundary Oxidation

Several remedies for stress accelerated grain boundary oxidation do exist. With varying degrees of success they include: changes in alloy chemistry, modified precipitation hardening heat treatments that alter the grain boundary microstructure, thermomechanical

processing, or oxidation resistant coatings. Alloy chemistry modifications are geared towards producing a stable oxide layer or adding beneficial grain boundary segregants. [32] Although this last remedy may seem to be the most straightforward solution to the stress accelerated grain boundary oxidation problem, retaining a low α_m places constraints on how far the alloy chemistry can be successfully modified. In high temperature aerospace applications with relatively narrow operating temperature ranges, any compromise in an alloy's α_m may be unacceptable.

The Cable-In-Conduit-Conductor application is a good example of a limited high temperature exposure (Nb₃Sn heat treatment) that lends itself to a broader range of alloy chemistries. This is because the large temperature range (1000K to 4K) involved and greatly extended low temperature regime produce less of an overall effect on α_m . If the expected maximum service temperature is low enough (below or near T_i), up to 5 wt.% chromium can be added to these alloys to give improved resistance to stress accelerated grain boundary oxidation. [30] Addition of 2 wt.% Cr to an experimental Ni-Fe-Co base low coefficient of expansion superalloy, in combination with a modified grain boundary microstructure, has been shown to double the stress-rupture life over a similar chemistry alloy without Cr. [33] When compared with alloy 903, the same alloy showed a 2000 fold increase in stress-rupture life. Adding 5 wt.% Cr to another Ni-Fe-Co base low coefficient of expansion alloy improved both its overall oxidation resistance and stress-rupture life. [34] In the development of alloy 908, the temperature range of interest, 4K to 1000K, permitted the addition of 4 wt. % chromium with a tolerable increase in α_m over that temperature range. [1, 2]

E. Microstructural Characteristics of Low Coefficient of Thermal Expansion Iron-Nickel Base Superalloys

In position among other nickel-iron-base superalloys, the low coefficient of thermal expansion superalloys are either γ (ordered fcc [Ni₃(Al,Ti)]) strengthened, (alloy 908 and alloy 903) or γ' (bct Ni₃Nb) strengthened, (alloy 905). [1, 3] Although the exact nature of the strengthening phase has not been reported in the literature, alloys 907 and 909 have high (Ti+Al)/Nb ratios, that promotes γ' strengthening. [35] The precipitate formed in these alloys is dependent upon the percentages of Nb, Al, and Ti present. Alloys such as 905, 907, and 909 have low Al contents. [30, 36] To compensate for the low Al levels and

maintain the same volume fraction of strengthening phase(s), the amount of Nb is increased. Because of this, these low coefficient of thermal expansion iron-nickel base superalloys also exhibit relatively dynamic intergranular microstructures, with corresponding variable grain boundary chemistries in the SAGBO temperature regime. The role of intergranular precipitates in oxygen embrittlement in the 550°C to 800°C range, either through their effect on local chemistry or oxidation of grain boundaries, has not been fully explored.

F. Stress Accelerated Grain Boundary Oxidation and Alloy 908

Present interest in stress accelerated grain boundary oxidation, from a cryogenic materials viewpoint, stems from research leading to the development of alloy 908 as the sheathing material used on the US-DPC magnet. [1, 3]

Stress-rupture tests performed during the development stage of alloy 908 showed that the addition of 4 weight percent Cr improved its notch-rupture behavior in air over that of the extremely notch-sensitive alloy 903. [3] Experience has shown that a magnet constructed of alloy 908 can be successfully heat treated in vacuum. [14] Tolerance to degraded furnace environments, either vacuum or inert gas, had not been established.

Stress-rupture behavior of alloy 908 at high temperature in air show characteristics that indicate its susceptibility to stress accelerated grain boundary oxidation. [37]. While the data indicated adequate life expectancy in air for very low stress levels (< 200 MPa), the actual stresses in the pre-heat treatment conduit, from plastic deformation during conduit fabrication and from magnet winding, have not been established. This is because a wide variety of possible fabrication methods and magnet designs are under consideration. It is anticipated that residual stresses from tube forming and/or extrusion, winding and elastic strains due to constraining the coil after winding will be present. For the magnet designers, a map of the stress accelerated grain boundary oxidation regime for alloy 908 in terms of stress, time, and furnace atmosphere, will be essential for the successful heat treatment of large scale Cable-In-Conduit-Conductor magnets.

There is no question that such structures can be successfully heat treated in vacuum. For economic reasons, however, very large scale magnets, such as those to be designed for the International Thermonuclear Experimental Reactor (ITER), heat treatment in an argon atmosphere may be considered. The problem with this approach is that the oxygen concentrations in inert gases may exceed the threshold level for alloy 908.

The goal of this study is threefold. First, from the perspective of Cable-In-Conduit-Conductor magnet heat treatments, is to determine what level of environmental control over

oxygen concentration is required to prevent intergranular cracking. Second, and more basically, what is the relationship between oxygen concentration, stress and temperature that leads to intergranular failure in this alloy? And lastly, the role of the above variables as related to the fundamental mechanism of stress accelerated grain boundary oxidation cracking. The effect of modification of surface residual stresses on stress accelerated grain boundary oxidation will also be examined.

The following literature review will cover the extent of research into oxygen embrittlement phenomena in Ni-Fe base superalloys. An interesting point of comparison is that the heat treatment temperature selected for the International Thermonuclear Experimental Reactor conductor, 650°C, corresponds to the prevalent temperature used for high temperature gas turbine materials research. The difference is that the International Thermonuclear Experimental Reactor magnet coil will be required to undergo a single cycle high temperature exposure corresponding to Nb₃Sn heat treatment, while the turbine materials face multiple cycles over their lifetimes.

II. LITERATURE REVIEW

When the literature is reviewed with respect to the specific topic of stress accelerated grain boundary oxidation in low coefficient of expansion iron-nickel base superalloys, there appears to be a dearth of information on this specific phenomenon. When the search is expanded to cover the area of oxygen embrittlement in fcc materials in general, and Ni or Ni-Fe base superalloys in particular, a large area of research that has developed in the past two decades emerges.

There are three primary areas of research that deal with oxygen's intergranular behavior. The first of these are studies that are concerned with the effect of oxygen embrittlement on high temperature fatigue, creep and stress rupture in Ni and Ni-Fe base superalloys. Second are intergranular oxidation studies covering a range of materials. In many aspects, these first two areas overlap. Finally, research into intergranular embrittlement by oxygen of $\text{Ni}_3(\text{Ti},\text{Al})$ intermetallics has followed a somewhat parallel course to that of superalloys. The primary focus of this review will be the first of these topics, as it has the most direct connection with low coefficient of expansion iron-nickel base superalloys. Coincident research in intergranular oxidation and intermetallics will be covered where applicable to stress accelerated grain boundary oxidation and points of similarity reviewed. This review is organized in a semi-chronological order that traces the development of understanding of oxygen effects on material properties. The nominal compositions of the superalloys mentioned in this review are given in Table 1A in the Appendix.

The phenomenon of oxygen induced embrittlement in materials had been recognized early on to explain differences in mechanical behavior between vacuum and air. While the success of most high temperature alloys has not been hampered by its existence, there are different degrees to which this phenomenon manifests itself, depending upon the material.

The list of Ni and Ni-Fe base superalloys that have been reported to exhibit intergranular oxygen effects is fairly extensive. With respect to the effect of oxygen on fatigue fracture, two reviews provide a fairly wide coverage. Ericsson provides an extensive listing of researchers and materials studied, in which the effect of oxygen on fatigue fracture has been examined. [38] Gell and Duquette have reviewed some of the proposed mechanisms for oxygen's effect on fatigue fracture. [39] A more recent work by Pineau provides an update on some of these mechanisms and provides a more specific overview of oxidation related mechanisms. [40]

A. Fatigue Crack Growth Rate in Air Versus Vacuum

Early studies on fatigue crack growth reported on the interaction of oxidation processes with dislocation motion that prevents slip band reversal. [41, 42] Other researchers reported higher crack growth rates for fatigue tests performed in air compared with those performed in vacuum. [43, 44] The effect of oxygen can be seen on transgranular and single crystal crack growth rates, as well as intergranular crack growth. [39] . In examining these studies, it is important to distinguish between intergranular and transgranular effects. The stress accelerated grain boundary oxidation phenomenon in low coefficient of expansion iron-nickel base alloys is essentially an intergranular effect, so the following discussion will center on behavior leading to increased intergranular crack growth rates.

Intergranular crack growth during fatigue loading is encountered at high temperatures (above 500°C), in combination with oxygen containing environments and low frequencies (≤ 0.05 Hz). [45, 46, 47, 48, 49, 50, 51, 52] Similar environmental effects have been found in creep crack growth studies on Ni-base and Ni-Fe base superalloys. [46, 53, 54, 55, 56] The fatigue crack growth process is time dependent if it increases with increasing temperature and/or decreasing frequency, at which time the crack path changes from transgranular to intergranular. [57] In contrast to dynamic loading, under static loading, the crack growth processes are completely time dependent. Sadananda, et al., reviewed the effects of test variables and environment on crack growth in Ni-base superalloys. [58] The time dependent fatigue crack growth regime is where intergranular stress assisted oxidation is found to occur. Merrick, et al., observed significant increases in crack growth at low frequencies at 650°C in Waspaloy and P/M Astroloy. [46] The increased fatigue crack growth rate was associated with a transition to intergranular crack propagation. This is illustrated in Figure 2 that shows how the crack growth mechanism changes with frequency and temperature in air. Oxidation assisted fatigue crack growth rate in alloy 718 at 650°C increases as the fatigue frequency is decreased, and when a tensile hold time is superimposed on the fatigue cycle. [45, 47, 48, 50, 54, 51] Pédrón, et al., attributed these results in alloy 718 to stress-assisted oxidation. A plot of their da/dN versus frequency data is shown in Figure 3, to illustrate the effect of decreasing frequency. The slope of the da/dN versus frequency curve at low frequencies, and 650°C was found to close to -1. [47] This indicates that at low frequencies the fatigue crack growth rate is time dependent. As occurs in corrosion fatigue, the reason that time dependency becomes prevalent at lower

frequencies is because there is more time for environmental attack to occur. The plot shown in Figure 4 illustrates the effect of hold time on the fatigue crack growth ratio $(da/dN)_{hold}/(da/dN)$. The mechanical and environmental variables found to influence fatigue crack growth in alloy 718 have been catalogued in two recent review papers by Ghonem, et al. [51, 59]

Floreen and Kane performed an extensive study on the effects of many different furnace environments on fatigue crack growth in alloy 718. [60] Their test methodology utilized low frequency (less than 0.1 Hz) fatigue loading to study environment-dependent crack growth. Another factor considered in their study was the water vapor concentration in the test atmosphere. Here, Floreen and Kane found that relatively high amounts (50,000 ppm) of water vapor in He produced fatigue crack growth rates comparable to those in 100 ppm oxygen in He. The same amount of water vapor in hydrogen gas produced fatigue crack growth rates between those of air and helium. The addition of water vapor to air did not result in any significant increase in fatigue crack growth rate. They concluded from He plus oxygen and the He plus water vapor tests that oxygen was produced by the reaction between the alloy and water vapor, and was responsible for the increase in fatigue crack growth rate. [60] Gell, et al., showed no difference in cycles to failure in wet versus dry air in single crystal MAR-M200. [39] The same material showed large differences between air and vacuum behavior. [39]

B. Tensile Embrittlement and Stress Rupture Life

Results from Chang's early research showed high temperature tensile embrittlement of several Ni-base superalloys. He attributed this embrittlement to interactions between grain boundary γ' and oxygen. [61]

In a series of papers, Woodford and Bricknell examined the effect of intergranular oxygen diffusion on the tensile embrittlement in different purity grades of Ni. [62, 63, 64, 65] Their test methodology involved very high temperature (1000°C) air or vacuum

Figure 2. Crack growth rate in air as a function of temperature at, $K_{\max} = 40 \text{ MPa}\sqrt{\text{m}}$, showing the change in micromechanism of crack growth with changes in frequency. T_{tm} = Mixed mode to intergranular transition temperature. T_{mc} = Mixed mode to transgranular transition temperature. From Ghonem, et al., [51]

Figure 3. Variation in fatigue crack growth rate with test frequency and temperature for alloy 718 at 550 and 650°C ($\Delta K = 40 \text{ MPa}\sqrt{\text{m}}$). From Pedron, et al., [47]

Figure 4. Effect of a hold time applied at zero load on the fatigue crack growth rate ratio $(da/dN)_{\text{hold}}/(da/dN)$ in alloy 718. From Pineau. [40]

exposure followed by tensile tests in argon (>99.996% Ar) at temperatures ranging from 25 to 1000°C. Through the use of a series different test atmospheres they identified oxygen as the embrittling species. The effect of oxygen on the temperature dependence of tensile embrittlement was postulated to be the result of decreased grain boundary mobility as a result of oxygen penetration. [62, 63] The intergranular fractures and metallographic cross sections produced in their experiments showed clear signs of grain boundary cavitation. Based on experimental results for Ni, they surmised that cavity formation was the result of the gaseous byproduct of a reaction between carbon and oxygen, and occurred at oxygen partial pressures below those at which NiO is stable. [64] The same work reported general internal oxidation along with the formation of grain boundary oxides. Pandey, et al., reported reductions in creep life in alloy X-750 that they attributed to intergranular cavity formation at low $P(\text{O}_2)$. [66] Although metallographic cross sections from this work showed clear intergranular oxidation, no fracture surfaces were shown to confirm that intergranular cavitation had occurred. In addition to studies on Ni, Bricknell and Woodford also examined the effect of prior air exposure on the stress rupture life of some Ni-base and Co-base superalloys. [67, 68] Woodford found that prior exposure in air at 900 and 1000°C of the cast alloy 738 resulted in severe loss of ductility and rupture life. [68] An important finding from this study that may have application to low coefficient of expansion iron-nickel base superalloys is that Co-base coatings (CoCrAlY) were found to

be more effective at preventing oxygen damage than Ni-base coatings. Related to this study was the finding, based on stress rupture and tensile tests, that Co-base superalloys are somewhat immune to oxygen damage. [67] In one of the first comprehensive studies on low coefficient of expansion iron-nickel base superalloys, Bricknell and Woodford proposed an alternate mechanism for stress accelerated grain boundary oxidation in these alloys. [28, 29] From their analysis of samples that had received comparable high temperature air or vacuum exposure prior to testing, Bricknell and Woodford proposed an alternate mechanism. They suggested that a grain boundary is first embrittled by intergranular oxygen diffusion, the embrittled grain boundary fails in tension, and the newly-exposed surfaces are then oxidized. [28, 29] The process propagates as oxygen diffuses down the grain boundary ahead of the crack tip, embrittling the next segment of grain boundary. This was based on their observation that there was no preferential grain boundary oxidation of these alloys in the absence of stress, i.e., no intergranular oxidation preceding cracking. Of most importance is the link their work provided between the oxygen effects in high temperature fatigue and creep behavior to the stress accelerated grain boundary oxidation phenomena in low coefficient of expansion iron-nickel base superalloys. [32] Their mechanism can be compared to the earlier mechanism suggested by McMahon and Coffin. [31] The mechanism they proposed starts with intergranular oxidation. The intergranular oxide then cracks in tension, allowing new oxide to form at the crack tip, with the process then repeating itself. A schematic illustration of the two mechanisms is shown in Figure 5.

One problem with using Bricknell and Woodford's analysis of this phenomenon is that they utilized high temperature (100 hours at 1000°C) air exposure, essentially in the realm of intergranular oxidation, prior to testing. [28, 29] Since no TEM studies on this particular alloy were included, it cannot be assumed that intergranular oxidation had not occurred during the high temperature exposure. Although tests were performed on samples in which the internal oxide zone was machined away, as will be discussed in a coming section, intergranular oxidation can extend beyond the internal oxide zone. Also, based on their work with oxygen embrittlement in Ni, they dismissed any direct role of grain boundary microstructure in superalloys as being necessary for oxygen embrittlement. Subsequent work by other researchers has shown that grain boundary microstructure does play an indirect role in oxygen embrittlement, and this topic will be discussed next.

Figure 5. Schematic comparison of stress accelerated grain boundary oxidation cracking mechanism proposed by McMahon and Coffin and that proposed by Bricknell and Woodford.

C. Role of Microstructure and Alloy Chemistry

The role of grain boundary microstructure appears to influence oxygen embrittlement in two ways. First, and most directly, grain boundary phases act to getter oxygen diffusing along the grain boundary by oxidizing. Second, and less directly, the precipitation and growth of intergranular phases alters grain boundary chemistry, and hence oxidation characteristics.

Pédrón, et al., reported three microstructural features in alloy 718 that reduced the creep crack growth rate in air. [47] Those were increased grain size, coarsening of the γ' (Ni_3Nb) strengthening precipitate, and intergranular precipitation of orthorhombic δ (Ni_3Nb). Chang found that a deformed grain structure in alloy 718 reduced the fatigue crack growth rate but found less grain size dependence. [50] Floreen, et al., reported that overaging of alloy 718 reduced both the fatigue and creep crack growth rates. [45] Coarse grain size has been reported to reduce crack growth rates. [46] Oxidation of primary (Nb,Ti)C carbides has been observed in many superalloys, and it has been suggested that preferential carbide oxidation may be a factor that contributes to grain boundary embrittlement. [31, 56, 69]

Woodford found that hafnium and boron additions to alloy 738 alleviated the detrimental effects of oxygen. [68] Other work showed that boron added to Ni and alloy 903A segregated to grain boundaries due to its low matrix solubility and eliminated intergranular embrittlement. [28, 29, 65] Chang reported that Cr additions to alloy 718 improved cracking resistance in the time dependent fatigue crack growth regime. [50].

Early work by Wilson examined the effect of microstructure on stress-rupture properties of alloys 718 and Waspaloy. [70, 71] He reported time-dependent notch sensitivity in the temperature range of 482-649 °C, with cracking occurring in the intergranular mode. Overaging resulted in reduced notch sensitivity. In alloy 718 the overaging treatment that resulted in improved properties introduced intergranular δ (orthorhombic Ni_3Nb) phase. These results were similar to those of Pédrón discussed above. Other grain boundary microstructures can have detrimental effects on stress rupture properties. Reductions in stress rupture lives have been reported in Ni-base superalloys in which intergranular γ' precipitation occurs. [61, 72]

The experimental results cited above are of particular interest since changes in intergranular microstructure that have been reported to reduce fatigue and creep crack growth rates and improve stress rupture properties are similar to those used to reduce the

susceptibility to stress accelerated grain boundary oxidation of low coefficient of expansion iron-nickel base superalloys. Reducing or eliminating Al from low coefficient of expansion iron-nickel base superalloys appears to be somewhat effective in reducing the effect of stress accelerated grain boundary oxidation. [30] This is an indirect benefit that appears to result from increasing the concentrations of the other hardening elements, Nb in particular. This makes the alloy's microstructure more susceptible to overaging by changing the strengthening precipitate from γ' to γ'' . The higher Nb concentration results in a complex, intergranular microstructure containing Nb-rich phases. It is for this reason that alloys 905, 907, and 909 have reduced levels of aluminum. [30] Alloy 907 (also designated 903A), for example, depends upon its low aluminum content (less than 0.1 wt.%) and heat treatment to generate Nb-rich intergranular phases to improve stress rupture life. [30] Adding Si to alloy 909 has improved the notch rupture strength of this alloy. Studies suggest that the improvement in stress accelerated grain boundary oxidation resistance was due to the formation of intergranular iron silicides. [36] Recently, it has been found that stress accelerated grain boundary oxidation resistance could be improved by increasing the Al content to above 5 wt.%. [73] This improvement was correlated with the formation of coarse, intergranular β (bcc NiAl) phase.

Additions of boron, hafnium and zirconium have been shown to improve the resistance of low coefficient of expansion iron-nickel base superalloys to stress accelerated grain boundary oxidation, though their effectiveness appears to depend upon alloy chemistry. [28, 29, 30, 36, 74]

D. The Effect of Oxygen Partial Pressure

The composite goal of all the research categorized above was to attain an understanding of how the chemistry of oxygen and the affected grain boundary interacts to produce embrittlement. This is particularly important if oxidation is part of the embrittlement mechanism. Similar studies in aqueous systems appear to be more detailed with respect to understanding the various chemical relationships. [75]

The studies cited above have focused on changes that occur when testing is performed either in air versus vacuum or in air versus inert gas. One problem with the use of inert gas testing is that a finite oxygen concentration is present in most "inert" gases. Experiments that are more pertinent to understanding and controlling furnace atmospheres to prevent stress accelerated grain boundary oxidation in alloy 908 are those that have studied the

effect of changing the partial pressure of oxygen during testing. These studies are less numerous in the literature.

In most cases, the effect of changing oxygen partial pressure manifests itself as a sigmoidal curve, with the abscissa being the partial pressure of oxygen and the ordinate some mechanical test parameter. Typically, the upper and lower plateaus in these curves correspond to oxygen partial pressures above or below which the test parameter shows no change. An early study by Achter, et al., showed that the reverse bending fatigue strength of Ni and Type 316 stainless steel decreased with increases in oxygen pressure. [44] For Ni, they found a leveling off point in cycles-to-failure at oxygen partial pressures below 1×10^{-3} Torr at 300°C and below 1×10^{-4} Torr at 816°C. Smith, et al., observed a similar transition in the fatigue crack growth of type 316 stainless steel occurring near 5×10^{-4} Torr at 500°C and at approximately 1×10^{-3} Torr at 800°C. [43] The mode of cracking in this experiment was transgranular. Smith, et al., performed similar experiments on Ag and found a transition in fatigue crack growth rate at an oxygen pressure partial pressure of 1×10^{-2} Torr at 21°C. [76] Interestingly, a transition in fatigue crack growth rate was not observed at 350°C and was attributed to the instability of AgO at that temperature.

E. Effects of Oxygen Partial Pressure and Stress on Intergranular Oxidation

With the exception of the early studies described above, surprisingly few studies have been carried out to study the effect of oxygen partial pressure on fatigue or creep crack growth rate until relatively recently. Most of the recent research in this area has been focused on alloy 718, and many of the results from work on that alloy may be applicable to understanding the oxygen embrittlement phenomenon in alloy 908.

One of the most recent and complete studies that examined the effect of changing oxygen partial pressure on intergranular crack tip oxidation in fatigue was performed by Andrieu. [77, 78, 79] Similar to the results of earlier research described above, Andrieu observed a change in fatigue crack growth rate with changing oxygen partial pressure. A plot illustrating his da/dN versus oxygen partial pressure results is shown in Figure 6. As seen in this figure there are two transitions in da/dN , one between 1×10^{-3} and 1×10^{-2} Torr and the other near 1 Torr. The most significant result of this research is the proposal of a crack tip oxidation mechanism to explain the effects seen with changes in oxygen partial pressure. [78] Unlike earlier work, this research involved fairly detailed analysis of the oxidation products formed on fracture surfaces.

The mechanism they proposed is linked to the slow strain rate test results for 718 that showed an increase in the percent intergranular fracture surface with increasing oxygen

partial pressure. [77] These results are shown in Figure 7. A transition between all intragranular fracture and mixed transgranular/intergranular was found to occur between 1×10^{-4} and 1×10^{-3} Torr. The relationship between percent intergranular fracture and oxygen partial pressure is similar to the fatigue crack growth rate behavior observed for alloy 718 as a function of oxygen partial pressure. [79] These results were correlated with Andrieu's Auger analysis of oxides formed on electropolished surfaces of alloy 718 at 650°C. [77] In this analysis, the composition of the oxide(s) formed was determined as a function of oxygen partial pressure. The results are illustrated in Figure 8. [77] The transition time was not quantified but estimated to be equal to 1000 s for alloy 718. This value was based on the fatigue loading hold time after which there was no further increase in the crack growth rate. This hold time was termed the "oxide saturation" time by Andrieu. [78] The curve shown in Figure 4 illustrates the plateau in fatigue crack growth rate with increasing hold time after 1000 s. Fatigue loading hold time experiments on alloy 718 latter determined the "oxide saturation" time to be 600 s. [78]

Based on the similarity in the surface oxidation behavior and the sigmoidal shape of the percent intergranular fracture versus oxygen partial pressure curve a two-stage oxidation was hypothesized. In the proposed mechanism, at high oxygen partial pressures, the first stage of oxide formation would be predominated by the formation of FeO and NiO and their spinels. [78] This is shown in the Auger results in Figure 8. After a transition time, T_p , the porous (Ni,Fe)O external oxide would reduce the oxygen partial pressure at the (Ni,Fe)O-metal interface low enough for Cr-rich oxides to be favored. The kinetics of this process depends upon; the diffusion rate of oxygen through the porous (Ni,Fe)O, temperature, $P(O_2)$, and localized stress and strain. [78] After the transition time, the Cr-rich oxide sublayer is fully developed and passivates the material by blocking further oxygen diffusion. A related diagram is shown in Figure 9 and illustrates the effect of surface preparation on oxidation of alloy 718. [40] As seen in this illustration, imposing a compressive residual stress on the surface of alloy 718 favors the formation of Cr-rich oxides over the entire oxygen partial pressure range. In contrast, mechanical polishing results in the formation of duplex oxide types with the same oxygen partial pressure dependency seen for electropolished surfaces. Ghonem and Zheng have developed a model that attempts to quantify many of the above experimental observations. [80, 81] In correspondence to Andrieu's work, they invoke a two-stage oxidation process to explain fatigue crack tip oxidation. Their proposed model depends upon the rate of formation of Cr-rich versus that of other oxide types. In this model, the rate at which Cr-rich oxides form depends upon both the intergranular diffusion of oxygen and the transport of Cr from the alloy matrix via a mobile dislocation network. [80]

Figure 6. Fatigue crack growth rate as a function of the oxygen partial pressure under constant ΔK (20 and 28 $\text{MPa}\sqrt{\text{m}}$) at 650°C in alloy 718. From Andrieu, et al. [79]

Figure 7. Percent intergranular fracture in alloy 718 slow strain rate test ($8.3 \times 10^{-4} \text{ mm/s}$) at 650°C versus oxygen partial pressure. Data from Andrieu. [77]

Figure 8. Results of oxide identification by Auger spectroscopy on electropolished specimens of alloy 718, showing transition time, t_P , between both forms of oxides as a function of oxygen partial pressure. From Pineau. [40]

Figure 9. Influence of residual stresses on the transition in oxidation mechanism. Cr-rich oxide is preferentially formed on shot peened specimens of alloy 718 at 650°C. From Pineau. [40]

F. Intergranular Oxidation

With the research cited above concerning oxide formation the relevance of controlled oxygen partial pressure becomes more apparent. Studies on Ni-Cr alloys provide some clues as to the effect of oxygen partial pressure and Cr concentration on intergranular oxidation. Rapp has classified the Ni-Cr system as Class 3. [82] Materials that fall into this class are dilute alloys of the base metals Ni, Fe, Co alloyed with Cr, Al, V, and Ti. [82] Because their oxidation behaviors fall into the same class, the oxidation of Ni-Cr alloys can be used to model oxidation of Ni and Ni-Fe base superalloys. [82, 83] The primary oxide types (NiO and Cr_2O_3) formed in this class are p-type, cation deficient. The surface oxide is formed by cation diffusion from the metal into the scale and then through the scale to the oxide/gas interface.

Intergranular oxidation can be defined as oxide formation at grain boundaries that extends deeper into an alloy than predicted by internal oxidation. [84] Internal oxidation is the process by which oxygen diffuses into an alloy and causes subsurface precipitation of the oxides of one or more alloying elements. [82, 85] The alloying elements that oxidize must form oxides that are more thermodynamically stable than those of the solvent metal. [86] For internal oxidation without external scaling, the oxygen partial pressure in the environment must be greater than that required to oxidize the alloying element but less than that required to oxidize the solvent metal. [85] Under internal oxidation conditions, grain boundary oxide precipitation is favored because grain boundaries are preferred nucleation sites and the oxidizable alloying elements may be segregated at the grain boundaries. [85] The combination of the low solubility of oxygen in Ni and the fast grain boundary path for oxygen diffusion promotes intergranular oxidation. Based on internal oxidation experiments, the lattice diffusivity of oxygen in Ni has been estimated to be $1.14 \times 10^{-11} \text{ m}^2/\text{s}$ at 1000°C , and approximately $4.27 \times 10^{-16} \text{ m}^2/\text{s}$ at 650°C . [87, 88] In contrast, the grain boundary diffusivity in Ni has been estimated to be on the order of $2.5 \times 10^{-12} \text{ m}^2/\text{s}$ at 650°C . [89] These estimates were obtained from Hwang and Balluffi's work. [89] Grain boundary diffusion of the oxidizable solute elements can also be expected to be faster than lattice diffusion. In a Ni-20 Cr alloy at 1000°C , for example, the ratio of tracer diffusion coefficients of Cr and Ni, $(D^*_{\text{Cr}}/D^*_{\text{Ni}})_{\text{g.b.}}$, equals 11. [90] For lattice diffusion in Ni-Cr alloys at 1020°C , $(D^*_{\text{Cr}}/D^*_{\text{Ni}})_{\text{lattice}}$ equals 1.7. [90] Also, as the temperature is lowered, grain boundary diffusion of Cr becomes more rapid relative to lattice diffusion.

Some general observations on the oxidation of Ni-Cr alloys will be enumerated before citing specific experimental observations on intergranular oxidation in Ni-Cr alloys.

- The critical minimum Cr content to ensure the formation of a protective surface oxide is approximately 20 to 25 wt.%. [91].
- The oxide growth rate for NiO is faster than that of Cr_2O_3 . [83, 92]
- The fast growing NiO nuclei overgrow the slower growth Cr_2O_3 nuclei. [83]
- An intermediate layer of the spinel NiCr_2O_4 forms. [82, 83]
- Preferential growth of the Cr_2O_3 layer down grain boundaries is linked to the short circuit diffusion path provided for Cr by the grain boundaries. [83, 91]
- The Cr_2O_3 sublayer grows laterally from grain boundary/surface intersections until it forms a continuous layer, this is illustrated in Figure 10. [83, 91]
- The surfaces of fine-grained materials develop better surface area coverage with Cr_2O_3 than large grain materials. A fine grain size results in more sites for diffusion of Cr and shorter lateral growth distances. [93]
- Growth of the Cr_2O_3 layer results in depletion of Cr from the matrix. [83, 91]
- For all Ni-Cr alloys with Cr mole fractions between 10^{-9} and 0.1, the concentration of Cr in the matrix at the Ni/NiO interface after internal oxidation should be approximately 10^{-3} ppm. [82]
- Between 800 and 1200°C and when the concentration of Cr is less than 5 wt.%, Cr_2O_3 is formed internally both at grain boundaries and within the interior of the grains. Under these conditions the alloy is covered by a NiO layer. [91]

Figure 10. Lateral growth of Cr_2O_3 layer originating from grain boundaries.

Research by Wood, et al., and by Shida, et al., has clarified the role of Cr in the intergranular oxidation in Ni-Cr alloys. [90, 94] Shida, et al., correlated the depth of maximum penetration of intergranular oxide with the depth of the Cr depletion zone in a Ni-40Cr alloy. [90] They postulated that the Cr depleted zone beneath the Cr_2O_3 layer allowed Cr_2O_3 to supply oxygen of sufficiently high activity to oxidize Cr deeper in the alloy. The generated oxygen penetrates down the grain boundary through a porous intergranular oxide to react with Cr and form Cr_2O_3 as an intergranular oxide. [90] A schematic based on their experimental results is shown in Figure 11. The voids formed at the matrix/oxidized grain interface were postulated to develop by vacancy injection as the Cr^{3+} ions incorporate into the oxide.

Figure 11. Intergranular oxide formation beneath a Cr_2O_3 surface scale. From Shida, et al. [90]

Wood, et al., examined Ni-Cr alloys with Cr concentrations ranging from 1 to 5 wt.%. [94] One general observation from their study was that grain boundary diffusion was more significant than lattice diffusion at low temperatures ($< 1000^\circ\text{C}$). Under low $P(\text{O}_2)$ conditions, they observed greater intergranular Cr_2O_3 formation than at high $P(\text{O}_2)$, where NiO formation was favored. [94] They tabulated the Cr concentration at the internal

oxidation/intergranular oxidation front as a function of alloy Cr content, time, and temperature. Their data are shown in Table 2. Intergranular oxidation also resulted in a Cr depletion zone adjacent to the oxidized grain boundaries. This was attributed to diffusion of Cr from grains adjacent to the grain boundary.

Table 2. Chromium Concentration In Dilute Ni-Cr Alloys at the Advancing Front of Internal Oxidation. From Wood, et. al. [94]

Test Condition	Alloy	Cr concentration wt. %
1100°C, 10h	Ni - 1% Cr	0.20
	Ni - 2% Cr	0.85
	Ni - 3% Cr	0.77
	Ni - 5% Cr	0.84
1000°C, 20h	Ni - 5% Cr	1.14
900°C, 40h	Ni - 5% Cr	2.25
800°C, 160h	Ni - 2% Cr	1.46
	Ni - 5% Cr	3.0

The composition and formation of intergranular oxides in Ni-15Cr-1.1Al alloys has been investigated by Stott, et al. [84]. They found the intergranular oxides that formed to be composed of Al_2O_3 , with Cr_2O_3 growing within the intergranular voids formed by vacancy annihilation at the intergranular oxide/matrix interface. [84] It was postulated that, for Al, the rate of diffusion down the grain boundaries was rapid. As a result, the diffusion of Al from the matrices of the adjacent grains was the rate limiting step for the formation of intergranular Al_2O_3 .

The transition from external to internal oxidation is of importance since it links the effects of changes in oxygen partial pressure to intergranular oxidation. According to Rapp, the transition from internal to external oxidation is a passivation process. [82] In the case of internal/intergranular oxidation, the reaction proceeds until sufficient intergranular oxide precipitates form to block further reaction between oxygen atoms and solute atoms. [82] Rapp demonstrated the effect of oxygen partial pressure on the external to internal oxidation transition in his experiments on Ag-In alloys. [82] In these experiments he varied both the concentration of the internal oxidant indium and the partial pressure of oxygen. His results are shown in Figure 12. The effect of decreasing the partial pressure

of oxygen and increasing the mole fraction of internal oxidant can be seen in this figure as promoting external oxidation or passivation. Based on these results Rapp suggested that preheat treatment of structural alloys at reduced oxygen partial pressures will produce a passivating external scale. [82] These results have been applied to Ni-Cr alloys. Wood, et. al., found that Ni-Cr alloys with higher Cr contents underwent a more rapid transition from internal/intergranular oxidation to external oxidation. [94] The oxygen partial pressure at the surface is also important. As the concentration of oxygen is decreased, a critical value is reached at which a transition from internal to external oxidation occurs. [94]

Figure 12. Transition from internal to external oxidation for Ag-In alloys at 550°C. From Rapp. [82]

The internal/intergranular oxidation experiments described above were generally static tests. Stress accelerated grain boundary oxidation also requires that the influence of stress on intergranular oxidation be recognized. In their study of Ni-Al alloys, Stott, et. al., and Shida, et. al., have found that intergranular oxidation is facilitated by stresses developed from the increase in volume produced when surface and internal oxides form. [95, 96]

This effect was most prominent at low temperatures (below 800°C), which the authors ascribed to the lesser extent of stress relief at that temperature.

It has been suggested that stresses generated by the formation of an internal or intergranular oxide are relieved by diffusion in the base metal. [97] The effect of an imposed tensile stress is to accelerate the rate of intergranular oxidation by helping to create space to accommodate oxide formation. [97] Emsley's, et al., study of 20Cr-25Ni-Nb stabilized stainless steel showed that the intergranular Si oxidation rate was controlled by the diffusion of Cr and/or Fe to the surface. [98] Mino, et al., found that intergranular oxidation of alloy 617 was enhanced under an applied tensile stress at 800 and 900°C [99]

G. Application to Stress Accelerated Grain Boundary Oxidation in Alloy 908

Susceptibility to the oxygen embrittlement phenomenon, by whichever mechanism, can be arranged by alloy group. The hierarchy of this arrangement would appear as,

{Ni aluminides > LCIN superalloys > Ni-Fe base superalloys $\geq$ Ni-base superalloys}.

In this ordering Ni aluminides (Ni_3Al) are the most susceptible to intergranular oxygen embrittlement. [100, 101, 102, 103, 104] The embrittlement research path in this material group parallels that discussed above for superalloys. Low coefficient of expansion iron-nickel base superalloys are next in line followed by the Ni-Fe and Ni base superalloys. Co-Cr base superalloys are not ranked because they are much less susceptible to oxygen effects due to their greater intrinsic ductility at high temperature. [32] The ranking listed above correlates well with decreasing amounts of Cr found in each material, 0 wt.% for Ni aluminides, 0-5 wt. % in low coefficient of expansion iron-nickel base superalloys, and 10 to 20 wt. % in superalloys.

One result suggested by these studies is that the addition of small quantities (< 10 wt. %) of chromium may not be of help to stress accelerated grain boundary oxidation. As most of the above research indicates, alloys with relatively high Cr concentrations (18 wt. %) experience similar oxidation assisted cracking. The one beneficial effect of having increased Cr levels may be in accelerating the rate of external oxidation (passivation). In the oxidation of Ni-Cr alloys, higher Cr contents translate to more rapid transition from internal to external oxidation.[94] Since stress accelerated grain boundary oxidation is an internal oxidation process, increasing the Cr content will, in effect, accelerate the formation of a passivating surface oxide. Chang's work on alloy 718 demonstrated this. [50] This is especially true if intergranular cracking occurs by the two-stage oxidation process

suggested by Andrieu. [77, 78, 79] One solution to stress accelerated grain boundary oxidation is increasing the concentration of Cr. Coefficient of expansion considerations restrict increases in Cr in low coefficient of expansion iron-nickel base alloys. In this case, reducing the diffusion rate of oxygen down grain boundaries may be of greater practical value. Grain boundary precipitation or segregation of oxygen getter phases and elements, respectively, is one example of this approach.

III. PROCEDURES

The effect of heat treatment atmosphere on intergranular cracking in alloy 908 will be examined through the use of controlled atmosphere notched stress-rupture tests. Normally utilized to establish the stress limits to be designed into components operating at high temperatures, this test method is also an indicator of a material's sensitivity to environmental damage in combination with stress concentrations.

Similar methods are used to conduct stress-rupture and creep tests. They both use similar equipment to measure the time to failure at a constant temperature and load. Stress-rupture tests usually run 1 to 1000 hours, allowing a full characterization of stress verses time to failure (rupture) in a shorter time span, as opposed to 1000 to 10,000 hours in creep tests. By design, stress-rupture tests focus on the time to failure, and do not provide for measurement of deformation during testing. By using a time-temperature parameter that correlates time, temperature, and stress, stress rupture data can be extrapolated to long times (decades) that are not feasible for testing.

The effect of modification of surface residual stresses on stress accelerated grain boundary oxidation will be examined using constant strain, C-ring tests. After surface modification the samples will be heat treated under known stress accelerated grain boundary oxidation conditions.

A. Material

The primary material used in this program was obtained in the form of 3.43 mm thick sheet (heat Y9401K) from INCO Alloys International Inc., Huntington, West Virginia. The material chemistry is given in Table 3. The processing history started with an electroslog remelted ingot 305 mm x 864 mm x length. The ingot was then hot rolled at 1121°C to 7.6 mm x 737 mm x length, followed by annealing at 954°C in a continuous anneal and pickling (CAP) line. This annealed form was then cold rolled to 3.43 mm x 737 mm x length and annealed in the CAP line at 982°C. This heat, with the addition of a final cold rolling step to obtain 5% cold-work, is the same as that used for air stress-rupture tests performed at INCO. [105]

The material used for the double notch round bar stress-rupture tests in this study had a different history and was obtained from heat Y9210 (chemistry given in Table 3). The processing steps followed for this material were vacuum induction melt, homogenize at 1191°C for 16 hours and fast cool. A series of forging and reheat steps produced approximately 25.4 mm thick plates that were mill annealed at 980°C for 1 hour. The final

processing step involved the cold rolling of strips cut from the plates to obtain 10 and 20% cold work. [37] The 20% cold work material was the same as that used by Nicol in his air stress rupture tests. [37]

Table 3. Compositions of Alloy 908 Used for Stress Rupture Testing.

Heat	Composition (weight percent)												
	Ni	Fe	Cr	Nb	Ti	Al	Si	Mn	C	Co	Mo	P	S
Y9401K	49.3	40.8	3.99	3.04	1.55	1.01	0.16	0.05	0.01	0.01	0.01	0.004	0.001
Y9210	49.5	40.9	3.86	2.99	1.57	0.97	0.13	0.04	0.01	—	—	—	0.001
HV5107	48.7	40.8	4.12	3.04	1.54	1.10	0.17	0.09	0.01	0.01	0.001	0.002	0.002

Additional double notch round bar samples were manufactured from heat HV5107 that started as a 21 kg vacuum induction melt ingot produced by INCO, chemistry given in Table 3. The ingot was homogenized at 1191°C for 16 hours, fast cooled, and then forged at 1191°C to plate 31 mm thick by 102 mm wide by 1170 mm long. The material was then annealed at 980°C for 1 hour and air cooled. Cold rolling introduced approximately 20% cold work.

B. Stress Rupture Test Procedure

The primary sample type used for argon atmosphere testing was a flat plate (3.15 mm thick) double-edge-notch design, for subsize sheet materials. The specimen geometry was chosen to closely replicate thin wall (< 3 mm) conduit designs. The notch produces an elastic stress-concentration factor (K_t) at the root of the notch of 4.5. A drawing of the specimen design is shown in Figure 13. Two sample orientations were machined for this sample geometry. One set of samples was machined so that their tensile axes were parallel with the longitudinal direction, with crack growth in the transverse direction, LT orientation. The other set was machined in the TL orientation, with their tensile axes parallel to the transverse direction and crack growth in the longitudinal direction. The LT oriented samples were the primary ones used for this study. The other sample type utilized is a double-notch-round-bar sample that incorporates the British standard V-notch with a $K_t = 4.1$. [106] This sample design is shown in Figure 14. To study the effect of heat treatment on stress rupture properties, several samples from both designs were heat treated in a 10^{-5} Torr vacuum at 650°C for 200 hours. All of these samples were in the LT orientation.

The test methodology closely followed ASTM E292-83 which provides a standard method for conducting time to rupture tensile tests for notched materials. [107] The stress rupture test matrix is shown in Table 4. The matrix was established first around stresses that would neither produce rapid tensile failure nor a stress rupture life in excess of 500 hours, dependent upon sample geometry. Using these stresses, the oxygen concentration and temperature were varied. An Applied Test Systems (ATS) lever arm test frame with auto load leveling and auto loading was used. The system incorporates an Inconel alloy 713 retort that serves as the environmental chamber. The retort is surrounded by a tubular, three zone, electric-resistance furnace with a programmable controller. To insure accurate temperature measurements, a thermocouple cold-junction compensator was used to monitor the temperature at the sample for the duration of the test.

Both oxygen and water vapor analyzers were used. A Delta F Corporation electrochemical process oxygen analyzer was used to measure oxygen concentration in gas sampled from the notch region of the test sample. As configured, the analyzer has a detection range of 0.01 to 50 ppm oxygen that was selected for sensitivity at low oxygen concentrations. Oxygen concentration in the testing retort was continuously measured by passing the exit gas through the analyzer at a flow rate of $5.66 \times 10^{-2} \text{ m}^3/\text{h}$ with an at gage delivery pressure of 129 Torr. The concentration of water vapor was measured with an EG&G analyzer that utilizes a phosphorus pentoxide electrochemical sensor.

Table 4. Test Matrix Used For Stress Rupture Tests. FP=Flat Plate Specimen(s), RB= Round Bar Specimen(s).

Temperature (°C)	Stress (MPa)				Oxygen (ppm)
	450	550	650	700	
550			√ FP		0.5 - 1
650			√ FP	√ FP	< 0.5
		√ FP	√ FP		0.5 - 1
			√ FP		3 - 6
			√ FP		33 - 53
			√ FP		195
	√ RB/FP		√ RB/FP		1000
700		√ FP	√ FP		0.5 - 1
					195
750	√ FP	√ FP	√ FP		195

1. Low Stress grind gage section.
2. Holes must be on centerline of reduced section within ± 0.002 ".
3. Notches to be centered in gage within ± 0.002 inches.
4. Notches are 0.0375 ± 0.001 " deep.
5. Notch root radius 0.006 ± 0.0005 ".
6. Remove all burrs and sharp edges.
7. Blank dimensions width not less than 0.750".

Figure 13 . Double edge notch stress rupture specimen, $K_t = 4.5$.

Figure 14. Double notch round bar stress rupture specimen $K_t = 4.1$.

Proper positioning of the two detectors with respect to one another was critical.

Arrangement in series on the exit gas posed a problem because the oxygen analyzer uses an aqueous electrochemical cell that produces a wet exit gas. Additionally, the water vapor analyzer produces oxygen as a byproduct of its electrochemical reaction. A parallel arrangement on the exit gas line was also ruled out since the oxygen analyzer requires a tight, no leaks, supply to maintain a constant oxygen reading with fluctuations of $\pm 2.8 \times 10^{-2}$ m³/h in the analyzer gas flow rate. Based on these considerations, the water vapor analyzer was placed in the supply gas line to the retort. This placement was acceptable since water vapor in the supply gas was being measured but not controlled for these tests, and in all cases the water vapor concentration of the supply gas remained constant throughout the tests.

For the argon tests, the gas was supplied to the retort using a high purity two-stage regulator. Either commercial argon gas of different grades or analyzed oxygen-argon mixtures were used to obtain the required oxygen concentration. Each new gas cylinder was sampled for oxygen and water vapor prior to testing. For low oxygen concentration tests (≤ 50 ppm), the standard procedure employed to attain a constant oxygen concentration was to continuously flow supply gas through the retort and supply lines at a 129 Torr regulator gage pressure until the oxygen concentration of the retort exit gas matched the initial cylinder reading. The time required to achieve this depended upon how long the retort and sample load train were exposed to atmosphere. To minimize contamination of other parts of the system, the supply and exit lines were kept shut and under argon during sample loading and cylinder changes. For high oxygen concentration tests (≥ 50 ppm) using pre-analyzed argon-oxygen mixtures, the retort was first purged with inexpensive 99.997 grade argon until the oxygen concentration from the retort matched that of the cylinder. The analyzed mixed gas was then introduced into retort for 30 minutes prior to testing. During the initial heatup of the retort and sample the oxygen concentration generally increased for the first several minutes as trapped oxygen and organics were baked out, but returned to the initial supply gas reading rapidly after that. Initial tests with low oxygen concentrations (< 1.0 ppm) showed that the new retort could significantly getter oxygen down to 0.01 ppm levels. This necessitated that the oxygen analyzer be placed on the exit gas side. Heating the retort in air at 1100°C to passivate it was not done, since a thick oxide coating would also serve as an effective oxygen and water vapor trap for future tests. A schematic of the arrangement of the equipment used in the experiment is shown in Figure 15.

Figure 15. Illustration showing of arrangement furnace, retort, and gas analyzers used for alloy 908 stress rupture tests.

The samples were cooled in the retort under flowing argon at the completion of each test. This prevented the fresh fracture surfaces from oxidizing. Every sample was examined using scanning electron microscopy (SEM) to establish failure mode and fracture morphology. In the case of the flat plate samples, SEM fractography was performed on one half of the fracture, the other was prepared for metallographic examination. Fractography of the round bar samples was done using SEM on one half of the failed notch, and the unfailed notch was prepared for metallographic examination. Metallographic sections for both sample types were made so that the view was of the plane parallel to the tensile axis. Samples for SEM and energy dispersive x-ray spectroscopy analysis (EDS) were prepared by diamond grinding to 20 μm followed by polishing with diamond suspensions down to a final 3 μm polish. To prevent charging near the mounting resin and at oxides, all the SEM samples were coated by vacuum evaporation of carbon. Samples used for grain size determination were immersed for 30 to 60 seconds in an etchant composed of 15 mL hydrochloric acid, 10 mL acetic acid, 10 mL nitric acid, and 6 drops glycerin.

A TOPCON ABT-150 scanning electron microscope equipped with a LaB_6 filament was used for the fractographic, microstructural, and chemical analyses. The ABT-150 is linked with a Noran Pioneer energy dispersive x-ray detector capable of light element detection. Semiquantitative analyses of collected spectra were performed using a Noran Voyager x-ray analyzer and software. Unless otherwise specified, spectra were collected at 15 kV and at a 17 mm working distance. The microscope was operated to give an approximate spot size of between 0.1 and 0.05 μm . [108]

Area measurements on fracture surfaces were performed from SEM micrographs with fractographic features manually traced into a Zeiss image analysis system. Grain diameter measurements were done in a similar fashion.

C. C-Ring Residual Stress Modification Study

A parallel study on the modification of residual stresses was performed. C-ring test samples manufactured from tubing were used. The material had been solution annealed at 980°C for 1 hour in a hydrogen furnace that left it in a bright condition, i.e., it was free of any surface scale or subsurface oxidation. The tube had a radius of 23 mm and a wall thickness of 3 mm. The grain diameter of the starting material was 73 μm . Samples were placed in test fixtures designed to produce $6.0 \pm 0.08\%$ plastic strain at the outer

surface of the C-ring. [109] The test fixtures were machined from alloy 908 to eliminate strain relief due to differential thermal expansion between the C-ring and fixture. An illustration of a test fixture with a C-ring in place is shown in Figure 16.

The test samples were divided into three groups; solution annealed (starting condition), stress relieved, and shot peened. The stress relief treatment consisted of heat treating the C-rings, in their test fixtures, in a 1×10^{-6} Torr vacuum at 650°C for 16 hours. The shot peened test samples were first mounted in their fixtures. The samples were then commercially shot peened using 230 mesh (maximum $63\text{ }\mu\text{m}$ diameter) steel shot at 10-12 A intensity, with 100% coverage of the exposed outer surface of the C-ring obtained. The test environment used to evaluate the samples consisted of a vacuum furnace with a degraded vacuum of 3×10^{-2} to 4×10^{-2} Torr (approximately 11- 8 ppm oxygen), measured by thermocouple gage. Heat treatment cycles were based on inspections for cracking that occurred after exposure intervals of 24, 70, and 200 hours at 650°C .

a

b

Figure 16. (a),(b) C-ring specimen holder designed to maintain a constant plastic strain of 6% during heat treatment.

IV. RESULTS

A. Microhardness and Grain Size

Heat Y9401K had a starting grain diameter of 13 μm . The grain size and orientation of the starting material is shown in Figures 17a and 17b. After stress rupture testing at 650°C, the grain diameters in several samples were measured and an average value of 14.5 μm was calculated. A micrograph showing the grain structure in one sample after stress rupture testing is shown in Figure 18a. Vacuum heat treatment at 650°C for 200 hours prior to testing did not contribute to further grain growth. The grain diameter for this condition, 14.2 μm , is essentially the same as that of the other stress rupture samples, as shown in Figure 18a. The 20% cold work material, heat HV5107, that was vacuum heat treated at 650°C for 200 hours, has a duplex grain size, as can be seen in Figure 18b. The small size grains that form the predominant volume fraction, have a diameter of 25.2 μm . The large grains in this material are essentially equiaxed, have a diameter of 200 μm , and show no texturing with rolling direction.

The 20% cold work material, heat Y9210, also has a duplex size distribution. In this material, however, the large grains were extremely elongated and oriented with the cold rolling direction. [37] The small size fraction had a grain diameter of 15.8 μm . The large elongated grains were acicular in shape and had a grain length, based on the c-axis of the grain, of 534 μm , the a-axis was of the same dimensions as that of the surrounding small equiaxed grains. The microhardness within any elongated grain was the same as that of the surrounding matrix. An etched metallographic sample of this material was heat treated at 650°C for 200 hours in a 1×10^{-6} Torr vacuum. This procedure was used to determine if the grains were unrecrystallized grains that had been elongated during the cold rolling operation and whether recrystallization would occur during stress rupture testing at 650°C. The optical micrograph shown in Figure 18c has had one elongated grain labeled with microhardness indentations. The same grain, after the vacuum heat treatment, can be seen in the SEM micrograph shown in Figure 18d. As can be seen by comparing these micrographs, the elongated grain did not recrystallize during heat treatment. As a microstructural feature these grains will, therefore, not change during stress rupture testing at 650°C.

Figure 17. (a) Grain size and orientation of 3.43 mm thick sheet starting material, heat Y9401K, used for the flat plate stress rupture test samples, grain diameter 13 μm , Hardness 266 HVN. (b) Grain size in stress rupture tested sample 61P (650°C/118 hours) grain diameter 14.8 μm , hardness 484 HVN.

Figure 18. (a) (b) Optical micrographs showing grain size in the flat plate sample 49P (14.2 μm diameter), and round bar (25.2 μm diameter) sample 1B, respectively, that had been vacuum heat treated at 650°C for 200 hours prior to stress rupture testing in 1000 ppm oxygen at 650°C. (c), optical micrograph of elongated grain in 20% cold worked material, heat Y9210, (d) SEM micrograph of the same area as in (c) after 650°C/200h vacuum heat treatment.

Growth of the γ' precipitate will occur during testing. The γ' growth rate for the cold worked material has been shown to be faster than for the solution annealed material. [1] A faster hardening response is therefore expected in the 20% cold work starting condition. In Figure 19, the evolution of microhardness for the two representative starting conditions, 980°C /1h solution annealed and 20% cold work, is shown along with that of the solution annealed flat plate and 20% cold work round-bar stress-rupture samples. The times given for the stress rupture samples in this plot represent the entire time at temperature for the samples, heat up to cool down, and are therefore longer than the times to rupture. As can be seen, the hardness values of the stress rupture samples fall between the aging lines for the solution annealed and the 20% cold work materials. Hardness values peak at approximately 200 hours, with little decline up to 1000 hours. The 20% cold work material hardens more rapidly. As had been previously reported, the 20% cold work material contains γ' prior to heat treatment. This, along with higher dislocation density, accounts for the rapid hardening response shown in this plot for this condition.[1]

B. Stress Rupture Results

Tables 2A and 3A, in the Appendix, contain a detailed tabulation of all the stress rupture test data. In Figure 20, the stress-rupture data are plotted to show the time to rupture versus stress for all the 650°C solution annealed samples tested in low/controlled O₂ in argon atmospheres. The argon atmosphere data have been grouped by oxygen concentration range for the flat plate samples to maintain plot clarity. These data are compared with air data generated at INCO Alloys International, Huntington, West Virginia for the same material heat but with 5% cold work applied before testing. The shift to increased rupture time for the low O₂ samples compared with the air data is immediately evident. Also evident is the grouping of failed, solution annealed low O₂ samples around a rupture time of approximately 108 ± 36 hours at 651 ± 18 MPa stress, as shown in Figure 21. The time to rupture in this stress range was independent of oxygen concentration, as is evident in Figure 21. The sample group for the 540 MPa stress range was insufficient (1 sample failed at 452.5 hours) to establish whether this independence of rupture time on oxygen concentration held at lower stresses.

The effect of test temperature, oxygen concentration, and stress for the flat plate samples can be seen in Figure 22. From this plot a general trend of increasing rupture life with decreasing test temperature can be seen and is expected. The mechanical properties of the material decrease and the creep rate increases with increased temperature. [110, 111]

Figure 19. 650°C HVN of all stress rupture test samples compared with the aging curves (solid lines) for solution annealed (980°C/1h) and 20% cold work starting conditions. Vacuum Heat Treat = 650°C/200h at 1x10⁻⁵ torr, FP = Flat Plate sample, RB = Round Bar sample, and CW = Cold Work.

Figure 20. Comparison of 650°C flat plate test sample stress rupture data for alloy 908 in argon with controlled oxygen concentration and the same heat treat of material but with 5% cold work and tested in air by INCO. [105] Arrows indicate specimens that did not fail, test stopped.

Figure 21. Distribution of times to failure versus oxygen concentration for flat plate samples tested at 650°C and in the stress range 651 ± 18 MPa. Times to failure are distributed around 108 ± 36 hours and are independent of oxygen concentration for this sample geometry.

Figure 22. Effect of temperature on time to rupture versus stress for solution annealed flat plate samples at 750, 700 and 550°C for different ranges of oxygen concentration.

Test results for the round bar material tested at 650°C in low/controlled O₂ in argon atmospheres are compared in Figure 23 with air data obtained for the same material heat by Nicol. [37] This plot shows several trends for this material and sample geometry. There is a substantial increase in rupture life with decreasing oxygen concentration. When compared with flat plate sample results, the effect of oxygen concentration on rupture life for the round bar samples is more pronounced, with better time to rupture separation for the 1000, 44, and 3 ppm O₂ samples. The effect of prior processing is also evident in this plot, with the solution annealed sample showing an extended life at 1000 ppm oxygen over the 20% cold work samples. No difference in behavior was observed for the 10% cold work sample tested at 1000 ppm oxygen and 469 MPa, and its time to rupture was within the range of the 20% cold worked samples tested under the same conditions.

Prior vacuum heat treatment resulted in no substantial change in rupture life for either of the sample geometries, as is shown in Figure 24. In one instance, a non-heat treated, 1000 ppm oxygen flat plate sample had a significantly longer rupture life than its heat treated counterpart, but they exhibited similar percentages of intergranular fracture at failure. The round bar samples, under identical conditions, ruptured within a short time of each other, as seen in Figure 24.

C. Effect of Oxygen Concentration

Optical and scanning electron fractography of failed and interrupted flat plate samples extended the picture of the influence of oxygen concentration on stress rupture test results. The relationship between oxygen concentration and percent intergranular fracture was first examined for the flat plate test data that formed the bulk of the testing done for this thesis.

Figures 25a and 25b show the macrographic character of a failed flat plate stress rupture sample tested in 6 ppm oxygen at 650°C and 640 MPa. For these samples, intergranular cracking proceeds along a flat front that extends in from the notch. Intergranular cracking from the sides was observed, but only in very limited areas and at shallow penetrations (1-10 grains deep) in samples tested at higher oxygen concentration. The concave areas in the region between the notches are the shear lips. The shear lip regions are slanted, have a smooth/ductile fracture appearance, and represent the predominant source of reduction in area observed in these samples. The crack paths along the shear lips are oriented 45° with respect to the tensile axis. An example of this can be seen in the notch cross-section of an interrupted 550°C test specimen shown in Figures 26a-c. The fracture morphologies observed in the flat plate test samples as a function of

Figure 23. Comparison of 20% cold work double notch round bar air data from Nicol [37] with low oxygen concentration test data for the same heat of material with 20% cold work, 10% cold work, and solution annealed starting conditions.

Figure 24. Comparison of time to rupture versus stress for vacuum (1×10^{-5} Torr) heat treated (650°C / 200 hours) then tested samples with samples tested in their as received condition. As received conditions, flat plate solution annealed and round bar 20% cold work.

Figure 25. Micrographs of 650°C sample 9P (640 MPa, 82.3h, 6 ppm O₂). (a,b) Stereomicrographs of reconstructed specimen after failure showing deformation pattern in region of notch.

Figure 26. 550°C sample 30P loaded at 644 MPa in 1.2 ppm O₂. Test stopped after 478.3 hours. (a,b) SEM micrographs showing exterior of sample at notch section. (c) Optical micrograph showing cross section of unfailed notch. Cracking observed in this sample was not intergranular in character.

oxygen concentration are illustrated in Figure 27. As shown in this illustration, two or three distinct fracture morphologies can be found in these samples depending upon oxygen concentration. Starting at the bottom figure, with no intergranular fracture originating at the notches, and moving up, with increasing oxygen concentration, the planar intergranular fracture region is seen to penetrate further into the sample from the notches. No evidence of ductility is observed on the intergranular fractures. The second fracture morphology seen in the flat plate samples, and in this illustration, is the V-shaped region extending into the sample from each notch. These regions are ductile with relatively large microvoids developed by creep cavitation. [112] Creep at the test temperatures employed in this study is possible in alloy 908 given that its' homologous temperature, T_h , at 650°C is 0.56 and 0.5 at 544°C. As illustrated, the V-shaped regions become smaller as the intergranular crack front progresses further into the sample. The semicircular areas in between are the shear lips that formed at final fracture. From a ductility or region of necking analysis, this illustration shows an increase in the pinned or brittle regions at the notches as the oxygen concentration is increased and a corresponding decrease in the shear lip areas. This observation is consistent with a decreasing percentage of shear lip area corresponding to increasingly brittle behavior. [113] In this case, intergranular embrittlement increases with increasing oxygen concentration. In cross section, the intergranular fracture path appears as a flat ledge perpendicular to the tensile axis. The length of the ledge corresponds to the depth of intergranular cracking, beyond which the crack path changes orientation and morphology to smooth/ductile along the shear lips. Based on fracture morphology, a plane stress condition exists for the flat plate samples examined in this study. An approximation of the plastic zone size for the flat plate samples was obtained from microhardness measurements in the vicinity of the notches of failed samples. Failed halves of test samples, with their longitudinal-transverse (LT) faces oriented for metallographic viewing, were used for the microhardness traces. The microhardness trace shown in Figure 28 starts at the rupture surface and runs in the longitudinal direction down the center of the sample to a distance of 7.8 mm. Subtracting the distance traversed over the shear lip, the plastic zone extends approximately 4800 μm (4.8 mm) vertically. This estimation is based on microhardness values that exceed the unstressed matrix value, shown in the plot as the double line. The transverse, notch to notch, microhardness trace is shown in Figure 29. Based on sample design, the notch to notch distance is 4.45 mm (4450 μm). The material between the notches has a higher microhardness than that of the unstressed matrix. This indicates that the plastic zone extends across this distance and overlaps for the two notches. This was verified on visual examination of these samples, and can be seen in Figures 25a

Figure 27. Characteristics of flat plate stress rupture fracture surfaces as a function of oxygen concentration.

Figure 28. HVN from microhardness trace along the longitudinal axis (tensile) of the stress rupture sample 5P (650°C, 652 Mpa, 44.1 hours, 53 ppm oxygen). Trace extends, in cross section, from the rupture surface down the center of the sample on the LT plane.

Figure 29. HVN from microhardness trace along the transverse axis (notch to notch) of the stress rupture sample 5P (650°C, 652 Mpa, 44.1 hours, 53 ppm oxygen). Trace extends, in cross section, from notch to notch, distance 4450 μm. Hardness values in this trace exceed that of the matrix away from the notch.

and 25b. The large plastic zone, relative to sample thickness ($r_p \geq t$), confirms that these samples were under plane stress conditions during testing and is consistent with fractographic evidence.

The actual fractographic characteristics observed with increasing oxygen concentration, as discussed above, can be seen in the SEM micrographs shown in Figures 30a-d. There is no correspondence between time to failure and increasing percent intergranular fracture. The micrographs shown in Figures 31a-f illustrate the effect of oxygen concentration on fracture characteristics at 650°C. Figures 31a and 31d show a fully ductile fracture that occurred after 96.4 hours in 0.01 ppm oxygen. In this sample, the grains at the root of the notch are deformed and evidence of some creep cavitation is present in the cross section view. [112] As seen in Figures 31b and 31e, testing in 0.75 ppm oxygen results in intergranular cracking that extends 2-3 grain diameters in from the notch, while the remaining material exhibits fully ductile fracture characteristics. When the oxygen concentration is increased to 53 ppm the intergranular fracture area increases to 41% and, as shown in Figures 31c and 31f, the intergranular fracture path has progressed along fronts parallel to the notches, and the remaining center band of material has failed in a ductile manner. The grains in the region that has failed in an intergranular mode are not deformed, as is evident in the cross section view seen in Figure 31c. A comparable set of 700°C fracture surfaces and cross section are shown in Figure 32a-d. At this higher test temperature the fracture surface shows more ductile area than the lower temperature samples at similar oxygen concentrations, but with typically shorter rupture lives. The alignment of creep cavities along the tensile axis is more prominent at this temperature, as can be seen in Figures 32b and 32d. This is the expected result of the increase in creep rate with temperature. The overall effect of increasing temperature on stress rupture fractography can be seen in Figures 33a-c for 750, 700, and 650°C tests. As can be seen in comparing these fractures obtained at identical stress (650 MPa) and oxygen concentration (195 ppm), the rupture time and percent intergranular fracture increase while reduction in area decreases with decreasing temperature. The ductile rupture component of the failure becomes more prevalent at higher temperatures when the other variables remain constant. [112]

No trend was observed between time to rupture and oxygen concentration. A definite correlation between oxygen concentration and percent intergranular fracture was observed. The data shown in Figure 34 are from flat plate stress rupture tests performed at 650°C and in the stress range 651 ± 18 MPa and at different oxygen concentrations. As can be seen in this figure, the percent intergranular fracture increases as the oxygen concentration or

(a) 1 ppm O₂, 8% Intergranular fracture

(b) 6 ppm O₂, 23% Intergranular fracture

(c) 38 ppm O₂, 40.4% Intergranular fracture

(d) 1000 ppm O₂, 58.5% Intergranular fracture

Fig 30. SEM micrographs comparing the intergranular fracture morphology in 650°C/650MPa samples as a function of oxygen concentration (a) 31P, 71.7h to failure, 1 ppm O₂, (b) 9P, 82.3h to failure, 6 ppm O₂, (c) 62P, 122h to failure, 38 ppm O₂, (d) 24P, 111.4h to failure, 1000 ppm O₂.

Figure 31. (a-c) Optical micrographs of notch fractures and (d-f) SEM micrographs of fracture surfaces for three 650°C samples. From (a,d) 4P (703 MPa, 96.4h, 0.01 ppm O₂), (b,e) 33P (650 MPa, 174h, 0.75 ppm O₂), and (c,f) 5P (650 MPa, 44h, 53 ppm O₂). Note that the grain deformation in (a) is extensive at the notch, (b) has intergranular fracture 2-3 grain diameters in from notch then deformed grains, and (c) has no grain deformation at notch and intergranular fracture extending 0.72 mm in from the notch.

Figure 32. (a) Sample 35P (700°C, 550 MPa, 27 h, and 0.95 ppm O₂) and (b) 6P (700°C, 640 MPa, 3.4 h, and 53 ppm O₂). Fully ductile fracture shown in (a) with creep voids present in cross section, grain deformation at notch. (b) Intergranular ledge at notch with no grain deformation visible in this zone, ductile zone after intergranular ledge shows grain deformation.

Figure 33. SEM micrographs showing the effect of temperature on fracture for a stress of 650 MPa and 195 ppm O₂. (a) Sample 65P, 750°C failure in 0.07 hours, 1.7% intergranular fracture. (b) Sample 64P 700°C failure in 1.6 hours, 40% intergranular fracture. (c) Sample 63P 650°C, failure in 114.2 hours, 47.8% intergranular fracture.

Figure 34. Percent intergranular fracture versus oxygen concentration for 650°C and 651±18 MPa stress range flat plate test samples.

partial pressure increases. As shown in Figure 35, a similar but inverse relationship is seen between the ratio of ductile fracture area to total area and oxygen concentration. Figure 36 shows a plot for all sample types (flat plate and round bar), in four starting conditions: solution annealed, 20% cold work, and either solution annealed or cold worked with the addition of a vacuum (1×10^{-5} Torr) heat treatment of 200 hours at 650°C. As can be seen from Figure 36, the curve develops a sigmoidal shape, with a low ppm oxygen transition at between 5×10^{-3} and 1×10^{-4} Torr, and a similar plateau as the oxygen concentration approaches that of air (760 Torr). This data is compared with the 650°C slow strain rate test results from Andrieu for alloy 718 in Figure 37. [77] As can be from this plot, both data sets follow the same trend, with the alloy 908 stress rupture data falling on top of those for alloy 718. With respect to oxygen concentration, the curve shape and transition points seen here also follow those seen in da/dN versus oxygen partial pressure and cycles to failure versus oxygen partial pressure curves for alloy 718. [40]

D. Interrupted Flat Plate Tests, Microstructure and Chemistry.

Crack morphology prior to final rupture was examined on several interrupted samples. The samples shown in Figures 38a-d illustrate this for the low stress (540 MPa) condition that produced extended rupture times, but percent intergranular fractures in the same range as high stress (650 MPa) samples at similar oxygen levels. An optical micrograph of the notch cross section shown in Figure 38a shows elongation of the notch section after 522 hours and some delineation of the grain boundaries at the notch due either to oxidation or precipitation. A SEM micrograph of the surface of the notch in this sample shown in Figure 38c. The notch in this figure shows evidence of intergranular tearing that is 1-2 grain diameters deep (20 μm). The notch cross section from a sample exposed to identical test conditions that failed at an earlier time (452 hours) is shown in Figure 38b for comparison. The notch cross section seen in Figure 38d is from a test that was stopped at 211 hours (0.9 ppm oxygen). There was no indication of intergranular cracking or grain boundary delineation in this sample. Internal oxidation was found to extend to a depth of 5-10 μm below the surface of the notch. A composition profile extending in from the surface of this sample was produced by EDS using spot analysis in the SEM. The profile was divided into element groupings to enhance its clarity and is shown in Figures 39 and 40. This composition profile shows several features. Most noticeable is the increase in niobium concentration extending 15 μm below the notch surface. Oxygen is present over the same depth. This indicates the association of the two elements in the form of an oxide.

Figure 35. Ratio of ductile fracture area to total fracture area versus oxygen concentration for flat plate samples at 650°C and 651.5 ± 18 MPa stress range.

Figure 36. Percent intergranular fracture versus oxygen concentration for all samples, flat plate and round bar, tested at 650°C and for all stress levels tested, range 535 ± 140 MPa.

Figure 37. Comparison of 650°C Inconel 718 slow strain rate (8.3×10^{-4} mm/s) tensile data from Andrieu [77] with 650°C notched stress rupture data from alloy 908 at 649 ± 18 MPa stress range.

Figure 38. Micrographs comparing the notch morphologies of the 650°C/540MPa samples (a) (c) 38P (0.5 ppm O₂ , 522 h test stopped), (b) 37P (0.5 ppm O₂ ,452 h failure) and (d) 8P (0.9 ppm O₂ , test stopped at 211h). Note elongation of notch in (a) compared with (d).

Figure 39. Energy dispersive spectroscopy composition profile of Fe, O, Ni, and Cr from the surface of the notch of sample 8P (650°C, 538 MPa, 211 h, and 0.9 ppm oxygen) obtained by SEM at 15kV and 4,000x magnification.

Figure 40. Energy dispersive spectroscopy composition profile of Fe, Ni, Nb, Ti, Al, and Si from the surface of the notch of sample 8P (650°C, 538 MPa, 211 h, and 0.9 ppm oxygen) obtained by SEM at 15kV and 4000x magnification.

The surface oxide found on this sample is 1-3 microns deep, and associated with this oxide is an enrichment in Cr, Ti and Al as seen in the 0-3 μm region of the profile shown in Figures 39 and 40. The presence of Cr, Al, and Ti in the surface oxide scale was expected since the oxides of these elements are the most thermodynamically stable and require only low oxygen activities to form. [86]

Although no clear grain boundary elemental segregation could be found in the short time, 211 hour, sample, further examination of the grain boundary delineation seen in the 522 hour sample was performed using SEM and EDS. The SEM micrographs shown in Figures 41a and 41b are from a region at the base of the notch shown in Figure 38a. The grain boundaries, as shown in these micrographs, are decorated with acicular and globular precipitates. The grain boundary precipitate region extends to a depth of 75 μm below the surface of the notch. The plots, shown in Figures 42 and 43, were obtained from a near surface (5 μm deep) region at the base of the notch using EDS. As was seen previously in the 211 hour interrupted test, the surface oxide is enriched in Cr, Ti, and Al to a depth of approximately 2 μm . Niobium enrichment can be seen to occur deeper below the surface starting at approximately 3 μm , along with a corresponding decrease in the concentration of Fe. To distinguish elemental segregation associated with the grain boundary delineation seen in this sample, an EDS x-ray map was obtained for the region shown in Figure 41b and can be seen in Figure 44. As can be seen from this map, the grain boundaries in this region show elevated levels of oxygen and niobium along with depletion of Fe. No clear pattern of segregation of the other elements was demonstrated by this technique. These results suggest that an oxide of niobium has formed at the grain boundaries. Another possibility is that a niobium rich phase such as niobium carbide formed at the grain boundaries. The niobium-rich phase gettered oxygen diffusing along the boundary, and then oxidized. [56, 69] Because this was a long time test, the latter explanation appears to be the most likely, given that long term heat treatments have been found to form a Nb rich intergranular phase in alloy 908. [1]

The intergranular fracture surfaces of all of the flat plate test specimens that ruptured had oxidized sufficiently to obscure fine microstructural details. Initially it was thought that this oxidation had occurred during the interim between failure and furnace cool down. **The ductile fracture surfaces resulting from final fracture did not show a detectable surface oxidation layer. The intergranular fracture surfaces did.** In order to examine how the fracture morphology and oxidation characteristics appeared prior to final fracture, a test was stopped before failure, cooled down, and fractured in air at

a

b

Figure 41. Flate plate 650°C sample 38P (0.75 ppm O₂, 542 MPa) test stopped at 522 hours. (a) Grain boundary microstructure at base of notch after test. (b) Higher magnification of region analyzed by x-ray mapping.

Figure 42. Energy dispersive spectroscopy composition profile of Fe, O, Ni, and Cr from the surface of the notch of sample 38P (650°C, 542 MPa, 522 h, and 0.5 ppm oxygen) obtained by SEM at 15kV and 15,000x magnification.

Figure 43. Energy dispersive spectroscopy composition profile of Fe, Ni, Ti, Nb and Al from the surface of the notch of sample 38P (650°C, 542 MPa, 522 h, and 0.5 ppm oxygen) obtained by SEM at 15kV and 15,000x magnification.

Figure 44. EDS x-ray map of grain boundaries at base of notch in 650°C sample 38P (0.75 ppm O₂, 542 MPa, 522 h). Segregation of oxygen and niobium at the grain boundaries is evident in the map. SEM micrograph of the region examined is shown in Figure 41b.

22°C. The sample, shown in Figure 45a-d, was exposed to 35.5 ppm oxygen at 650°C and 650 MPa stress before the test was interrupted at 188 hours. The exterior SEM micrographs in Figures 45a and 45b show cracking at the root of the sample's notch, and the cross section of the notch shown in Figure 45d shows the intergranular ledge at the notch. Area fraction measurements from Figure 45c showed there to be 19.4% intergranular fracture compared with 40% intergranular fracture seen in a failed sample at a similar oxygen concentration and stress. The SEM micrographs shown Figures 46a and 46b show the boundary between the intergranular and ductile transgranular fracture regions at low and high magnifications, respectively. The transition between intergranular and ductile transgranular is fairly abrupt as can be seen in Figure 46b. If it is assumed that the intergranular fracture occurred at temperature during testing, then it should show signs of surface oxidation, while the ductile transgranular fracture that presumably occurred at room temperature when the sample was broken open should be free of surface oxidation. The high magnification micrographs shown in Figures 47a-d were taken at the intergranular/ductile transgranular interface. The intergranular fracture surfaces shown in these micrographs are covered with a thin oxide layer. The ductile transgranular regions are not oxidized, indicating that ductile fracture occurred when the sample was broken open at 22°C. The presence of oxide free intergranular fracture surfaces at the ductile/brittle interface should be expected if it is assumed that the grain boundaries fail by intergranular oxygen embrittlement. If this were true, then this sample should have contained some, oxide-free embrittled intergranular fractures at the fracture interface. There was no evidence of oxide free intergranular fracture surfaces or cracks in this or any of the other test samples examined. This point will be developed further when the chemistry of the oxidized grain boundaries is discussed in the next section.

A related investigation involved placing companion, not loaded, (dummy) flat plate notched test specimens in the retort with loaded test specimens. At the conclusion of the test the dummy test samples were removed from the retort and fractured in air at 22°C. This test procedure was performed at 650°C and 700°C in 1 and 0.95 ppm oxygen environments, respectively. Optical micrographs of the notch cross sections and SEM fractographs of the 650°C loaded and dummy test specimens are shown in Figures 48a-c and Figures 48d-f, respectively. In Figures 48a,b and c the loaded test sample shows intergranular cracking extending in from the root of the notch, with no grain deformation in the intergranular fracture region. Comparable images of the dummy test specimen in Figures 48d, e, and f show elongation of the notch section before failure and no intergranular cracking in the SEM fractographs. Similar results were obtained for the 700°C dummy sample. **These results clearly indicate that the intergranular**

Figure 45. (a), (b), (c) SEM micrographs and (d) optical cross-section of notch from 650°C sample 60P (650 MPa, 35.5 ppm O₂). Test was stopped at 188 hours into test and fractured at room temperature, 19.4% intergranular fracture.

a

b

Figure 46. (a), (b) SEM micrographs from 650°C sample 60P (650 MPa, 35.5 ppm O₂) showing intergranular / ductile transgranular fracture transition. Test was stopped at 188 hours into test and fractured at room temperature, 19.4% intergranular fracture.

Figure 47. SEM micrographs (a-d) from 650°C sample 60P (650 MPa, 35.5 ppm O₂). Test was stopped at 188 hours into test and fractured at room temperature, 19.4% intergranular fracture. These micrographs have been taken from regions adjacent to the intergranular/ductile fracture interface, the ductile region is oriented to the right side in each micrograph.

Figure 48. (a,d) Optical micrographs of notch (upper right) cross-sections and (b,c) and (e,f) SEM micrographs of 650°C samples 31P and 32P. (a-c) Sample 31P tested at 640 MPa in 1 ppm O₂ and failed in 71.7 h. (d-f) Sample 32P was present in the retort with 31P but not loaded, it was fractured after the test in air at room temperature.

oxidation and fracture observed in this material requires a stress component and is not due solely to intergranular oxidation.

E. Round Bar Microstructure and Fractography

To obtain an intact notch at failure for microstructural and chemical studies double notch round bar test samples were utilized. Thus, the test atmospheres used were limited to a relatively high oxygen (1000 ppm) environment to produce rapid fractures with high percentages of intergranular failure, but without the gross oxidation of the fracture surfaces that limits detailed SEM and EDS analysis of material tested in air. The grain structure of this material, consisting of elongated grains with their c-axis parallel to the rolling direction of the plate, apparently had little influence on crack propagation. This is because the intergranular regions associated with these grains failed in the same manner as the equiaxed grains observed in the flat plate test samples. A good example of this is illustrated in the optical micrographs shown in Figures 49a-c. In these micrographs an elongated grain can be seen at the root of the unfailed notch in a round bar sample tested at 650°C in 1000 ppm oxygen. As can be seen in Figure 49c, the crack has started at the surface of the elongated grain and has propagated around it into the equiaxed grains behind it, and from that point the crack propagates into the sample in two branches separated by approximately 90°. An SEM micrograph of the fracture surface from a 20% cold work sample with elongated grains is shown in Figure 50. As seen in Figure 50, the fracture surface from this and all the other samples manufactured from this material show a texture corresponding to the orientation of the elongated grains. The same results were observed by Nicol in his air tests performed on this material. [37] A micrograph of a fracture surface from a sample manufactured from material without the elongated grains is shown in Figure 51. [1] Intergranular cracks in this material grow along a more planar front due to the absence of the large, elongated grains around which they must propagate. Comparing the two micrographs demonstrates that the texture seen in these fractures is due to the elongated grains.

In general, the cracks in the unfailed notches were closed with an intact oxide along the intergranular boundaries. One example of an intact crack can be seen in Figure 52a. This notch was not deformed or the crack opened when the second notch failed. The oxide present in the crack has been highlighted by vacuum evaporating carbon onto the sample then photographing it using Normarski interference-contrast illumination in a reflected light optical microscope. The main branches of this crack extend 0.6 mm into the sample. At

Figure 49. 20% cold-worked 650°C round bar test sample 20cw-31 (469 MPa, 7.3 h, 1000 ppm O₂). (a) Grain structure showing large, elongated grains parallel to the rolling and tensile directions. (b) Cross-section near unfailed notch showing elongated grain at the notch and crack path. (c) Detail of crack path around elongated grain at notch.

Figure 50. SEM micrograph showing the fracture surface of the failed notch from the 650°C round bar sample 20cw31 (469 MPa, 7.3 h, 1000 ppm O₂).

Figure 51. SEM micrograph of the failed notch in the 650°C round bar sample 1A (vacuum heat treated at 650°C for 200 h before testing at 469 MPa, 12.3 h, 1000 ppm O₂).

Figure 52. (a) Normarski optical micrograph of the crack path at the unfailed notch in the 650°C round bar sample 10cw2 (469 MPa, 8.2 h, 1000 ppm O₂), sample coated with evaporated carbon to highlight oxidized crack. (b) SEM micrograph from a portion of an oxidized crack path extending from the unfailed notch in the 650°C round bar sample 20cw31 (469 MPa, 7.3 h, 1000 ppm O₂).

higher magnifications in the SEM the finer intergranular crack branches appear black or dark gray, as seen in Figure 52b. This effect is due to the presence of low atomic number element(s) or compounds such as oxides at the grain boundary. The regions appear dark because there are fewer secondary electron scattering events, resulting in fewer secondary electrons reaching the detector. The next section will present the results of analyses of these grain boundaries.

F. Grain Boundary Analysis

Round bar test samples are preferred for grain boundary analyses. The intact notch they provide is desirable not only because it preserves pre-failure microstructural features, but also, for the purposes of this study, intact grain boundaries. Grain boundaries that have not cracked open provide evidence of pre-failure chemistry and intergranular oxidation, if present, without having direct exposure to the environment. In cases where intact notches were not available, i.e. flat plate sample, only those affected grain boundaries most distant from the notch were selected for analysis.

Metallographic etching removes grain boundary material. In analyzing the grain boundary chemistry of these samples, the grain boundaries were kept intact by automated mechanical polishing using diamond abrasives and polishes with no etching. The resulting surface is ideal for chemical analysis by EDS, but produces reduced contrast for imaging by SEM. As a result, the affected grain boundaries can be difficult to resolve. To enhance resolution carbon was vacuum evaporated onto the polished samples.

In order to establish which elements were predominant at the affected grain boundaries, an initial chemical analysis was performed by EDS using electron beam line scans across the grain boundaries. A line scan of the elements across two grain boundaries in a 650°C (1000 ppm oxygen, 4.05 hours) round bar sample is shown in Figure 53a. Oxygen is the only element that shows a definite peak at the grain boundaries, as seen from this line scan. An expanded oxygen line scan is shown in Figure 53b. Nickel and iron content show some reduction at the boundaries. To further define the grain boundary composition an EDS x-ray element map was acquired from a region near the notch in the same sample, and is shown in Figure 54. This map shows the segregation of oxygen to the grain boundaries, which are roughly outlined by the map. There is no segregation of chromium, titanium or aluminum to the grain boundaries. A reduction in nickel is evident. Iron is present at the boundaries and, in combination with oxygen, may indicate an iron oxide has formed there. The presence of a large, primary (Nb,Ti)C carbide is indicated in the upper left corner of the Nb and Ti maps. The presence of oxygen at the same location indicates that it has

Figure 53. (a) Line scan profiles of elements across two grain boundaries in the 650°C sample 1B unfailed notch (1000 ppm O₂, 4 hours). (b) Enhanced oxygen line scan. (c) Area used for line scan across two grain boundaries, cursor marks spot at one boundary.

Figure 54. EDS maps of the elements present at grain boundaries near root of notch in 650°C round bar sample 1B (650 Mpa, 1000 ppm O₂, 4 hours).

oxidized. The oxidation of niobium carbides has been shown to occur during intergranular oxidation of other superalloys. [55, 69] The grain boundaries examined above were close to the notch, and, hence, closer to oxygen present in the environment. Affected grain boundaries found further from the notch of the sample seen in Figure 52a are shown in Figure 55a. An enlarged oxygen x-ray map from this region is shown in Figure 55b. Oxygen is seen to outline the dark grain boundaries. A complete elemental map of the same region is shown in Figure 56. As seen in this map, no other element shows segregation to the grain boundaries in this sample.

The x-ray compositional maps generally lack sufficient resolution to distinguish small concentration differences among the elements. Electron beam spot analyses were performed at high magnifications across affected grain boundaries to detect compositional differences at grain boundaries. A 100 second analysis time was used for each spot to insure a good statistical ratio of x-ray counts for each element peak above background.

A 650°C round bar sample tested in 1000 ppm oxygen (4 hours) was selected for grain boundary analysis. As seen in the micrograph shown in Figure 57a, and previously discussed, the affected grain boundaries in this sample are dark in appearance. An EDS composition analysis across the grain boundary shown in Figure 57b was performed at 7,500x. The white points shown in the micrograph are electron beam contamination spots marking the path of the beam. From the resulting composition profile, shown in Figure 58, it is evident that oxygen is present on the grain boundary. Nickel, iron and niobium show some reduction at the boundary, while chromium appears unaffected. A reduction in the weight percent of these elements at the grain boundary indicates that they have oxidized. Reaction with oxygen reduces their relative weight percents in the formation of oxide to levels below those of the matrix. A grain boundary composition profile obtained at 20,000x from an identical sample tested at 650°C in 1000 ppm oxygen (12.3 hours), but at a lower stress, is shown in Figure 59. From the profile it is again evident that oxygen is present at the boundary and nickel shows some depletion at the boundary. In most cases, the composition profiles acquired across grain boundaries in the 650°C, 1000 ppm oxygen, round bar samples did not show segregation of Cr, Ti, Al, or Nb. This could be attributed to a combination of factors, one of which is the relatively small sample volume being analyzed. Grain boundary widths at these magnifications ranged from 0.1 to 0.5 microns. Another is that the electron beam spot size is of the same magnitude relative to the grain boundary width, one limitation of EDS analyses in the SEM even at their smallest spot size condition. Lastly, these elements may not be segregated at the grain boundaries in sufficient quantities to distinguish them from the matrix. Generally, a ± 0.5 weight percent difference is required. An increase in chromium and niobium was evident in a profile

a

b

Figure 55. (a) SEM micrograph and (b) oxygen x-ray map of grain boundaries in 650°C sample 10cw-2 (10% cold, work 1000 ppm O₂ , 469 MPa) 8.2 hours to failure.

Figure 56. EDS X-ray map of elements present along grain boundaries at the unfilled notch of 650°C, 469 MPa, 1000 ppm O₂, sample 10cw-2. An SEM micrograph of the selected region is shown in Figure 55.

a

b

Figure 57. Affected grain boundaries in 650°C sample 1B (1000 ppm O₂, 650 MPa, 4 hours to failure). (a) General region. (b) Grain boundary at triple point selected for EDS composition profile shown in Figures 58 and 59.

Figure 58. EDS composition profile across a grain boundary in the 650°C round bar sample 1B (650 MPa, 1000 ppm O₂, 4 hours to failure). Profile generated at 7,500x and 15 kV. An SEM micrograph of the grain boundary used is shown in Figure 57.

Figure 59. EDS composition profile across a grain boundary in the 650°C round bar sample 1A (469 MPa, 1000 ppm O₂, 12.3 hours to failure). Profile generated at 20,000x and 15 kV.

across the terminus of an affected grain boundary obtained at high magnification (20,000x). The composition profile for this sample is shown in Figure 60. Because of the very small grain boundary volume being analyzed, oxygen x-rays were detected but was not sufficiently resolvable above the EDS spectrum background for analysis. The dark coloration of the boundary, however, indicated that it was affected.

A series of composition profiles along, rather than across, grain boundaries was performed to investigate whether chromium was present at grain boundaries. A grain boundary at the tip of the crack path obtained from a flat plate sample tested at 650°C in 38 ppm oxygen (122 hours) is shown in Figure 61a. The boundary, along with electron beam contamination spots, is shown enlarged in Figure 61b. The resulting profile along the grain boundary is shown in Figure 62. As can be seen in this profile, oxygen is present along the entire length of the grain boundary. As the grain boundary terminus is approached from the matrix, however, it is apparent that the concentration of chromium increases. A similar but less pronounced increase in niobium can also be seen. From the grain boundary orientation in the micrograph (left to right) in Figure 61b, the matrix point used is closer to a branch of the main crack and the environment. Higher oxygen and iron levels are present along the segment of boundary closest to the main crack and the environment, while the chromium concentration increases away from the main crack. Andrieu reported similar findings in alloy 718 and attributed them to the initial formation of chromium rich oxides in low oxygen potential environments found at the tip of cracks. [77, 79] A companion composition profile taken across the chromium rich portion of the grain boundary is shown in Figure 63 and confirms the concentration increase. A composition profile was obtained from a second 650°C flat plate sample tested in 1000 ppm oxygen (28.3 hours) along the grain boundary shown in Figures 64a and 64b. From the profile seen in Figure 65, it can be seen that the chromium concentration along the entire crack has increased above the 4 weight percent level of the matrix. The concentration of niobium in the crack is also above the matrix level. Based on the composition profile, the oxide present at the beginning of the boundary, from where a grain can be seen pulled out in Figures 64a and 64b, is primarily an (Fe,Ni)O type oxide. A composition profile across the same grain boundary can be seen in Figure 66 and confirms the increase in chromium and oxygen. An analysis was performed on a round bar sample tested at 650°C in 1000 ppm oxygen (3.65 hours). The second notch in this sample had cracked open during testing and is shown in Figure 67a. The grain boundary selected for compositional analysis is shown in Figure 67b. From the profile for this boundary shown in Figure 68, it is apparent that in this sample there is no significant increase in the chromium concentration along the boundary. The profile does, however, show oxygen present along the boundary.

Figure 60. EDS composition profile across an affect grain boundary in the 650°C round bar sample 1A (469 MPa, 1000 ppm O₂, 12.3 hours to failure). Profile generated at 20,000x and 15 kV.

a

b

Figure 61. (a) SEM micrographs of oxidized grain boundaries in 650°C flat plate sample 62P (650 MPa, 38 ppm O₂, 122 hours to rupture). (b) Micrograph of grain boundary selected for compositional analysis by EDS.

Figure 62. EDS composition profile along grain boundary extending to terminus. 650°C flat plate sample 62P (650 MPa, 38 ppm O₂, 122 hours to failure). Obtained at 10,000x and 15 kV. Si, Ti, and Al did not show any variation in this profile and were removed for plot clarity.

Figure 63. EDS composition profile across grain boundary in the 650°C flat plate sample 62P (650 MPa, 38 ppm O₂, 122 hours to failure). Obtained at 10,000x and 15 kV. Si, Ti, and Al did not show any variation in this profile and were removed for plot clarity.

a

b

Figure 64. SEM micrographs of 650°C flat plate sample 49P (650 MPa, 1000 ppm O₂, 28.3 hour rupture time). (a) Affected grain boundary extending in from failed notch. (b) Grain boundary used for compositional analysis.

Figure 65. EDS composition profile along grain boundary in the 650°C flat plate sample 49P (650 MPa, 1000 ppm O₂, 28.3 hours to failure). Obtained at 12,000x and 15 kV. Si and Al did not show any variation in this profile and were removed for plot clarity.

Figure 66. EDS composition profile across grain boundary in the 650°C flat plate sample 49P (650 MPa, 1000 ppm O₂, 28.3 hours to failure). Obtained at 12,000x and 15 kV. Si and Al did not show any variation in this profile and were removed for plot clarity.

a

b

Figure 67. (a) SEM micrograph of crack at notch in round bar sample 20cw-24 (650 MPa, 1000 ppm O₂, 3.65 hours to failure). (b) SEM micrograph of grain boundary at the farthest distance from notch used for compositional analysis.

Figure 68. EDS composition profile along grain boundary in the 650°C round bar sample 20cw24 (650 MPa, 1000 ppm O₂, 3.65 hours to failure). Obtained at 12,000x and 15 kV. Si, Ti, and Al did not show any variation in this profile and were removed for plot clarity.

The results from this round bar sample are consistent with the previously reported findings based on x-ray maps and line profiles of affected grain boundaries in the other round bar samples tested at 650°C in 1000 ppm oxygen. With the exception of small increases at the very terminus of the affected boundaries, as was previously shown, significant segregation of chromium to the grain boundaries in round bar samples was not evident. Chromium enrichment is, however, evident along grain boundaries in comparable 650°C flat plate samples that were also tested in 1000 ppm oxygen. Aside from geometry, the main distinction between these two samples types is the time to failure, with the flat plate samples failing at longer times than equivalent round bar samples. Flat plate samples tested at lower oxygen concentrations also exhibited chromium concentrations at their grain boundaries that were from 2 to 10 weight percent above matrix levels. Chromium concentration was a function of position along the affected boundary, with the highest levels closest to the terminus.

G. Modification of Residual Stresses in C-Ring Test Samples

A compilation of the C-ring test results can be seen in Table 5. In this table, failure denotes intergranular cracking through the thickness of the ring. There were no failures among the six shot peened samples tested. Of the four stress relieved samples, none failed, and of the eight solution annealed samples tested, six, or 75%, failed. A macrograph of the failed C-ring S37 is shown in Figure 69a. As can be seen from this figure, the crack extends across the width of the C-ring at the apex of its ellipse. When the failed samples are broken open, the cracks can be seen to extend through the entire wall thickness, as shown in the SEM micrograph in Figure 69b.

Table 5. Alloy 908 C-Ring Test Results at 650°C, 6% Plastic Strain.

Sample Condition	Sample ID	Vacuum (Torr)	Exposure Time (hours)	Failure
Solution Anneal + Bend	S29	3×10^{-2}	24	yes
Solution Anneal + Bend	S37	3×10^{-2}	24	yes
Solution Anneal + Bend + Stress Relieve	S48	4×10^{-2}	24	no
Solution Anneal + Bend + Stress Relieve	S49	4×10^{-2}	24	no
Solution Anneal + Bend + Shot Peen	S13	4×10^{-2}	24	no
Solution Anneal + Bend + Shot Peen	S20	4×10^{-2}	24	no
Solution Anneal + Bend	S26	3×10^{-2}	72	yes
Solution Anneal + Bend	S27	3×10^{-2}	72	yes
Solution Anneal + Bend + Stress Relieve	S47	4×10^{-2}	70	no
Solution Anneal + Bend + Stress Relieve	S50	4×10^{-2}	70	no
Solution Anneal + Bend + Shot Peen	S22	4×10^{-2}	70	no
Solution Anneal + Bend + Shot Peen	S18	4×10^{-2}	70	no
Solution Anneal + Bend	S28	3×10^{-2}	120	yes
Solution Anneal + Bend	S38	3×10^{-2}	120	no
Solution Anneal + Bend	S1	4×10^{-2}	200	yes
Solution Anneal + Bend	S2	4×10^{-2}	200	no
Solution Anneal + Bend + Shot Peen	S16	4×10^{-2}	200	no
Solution Anneal + Bend + Shot Peen	S19	4×10^{-2}	200	no

Shot peening produces a thin layer of compressive residual stress to a depth of about one quarter to one half the shot diameter. [110] The dimpled surface texture produced by shot peening the C-ring samples can be seen in Figure 70a. A SEM micrograph showing the apex of the shot peened C-ring S13 after testing is shown in Figure 70b. As can be seen in this figure, and when compared to the failed C-ring in Figure 69b, no cracking was observed in any of the shot peened samples tested. A comparison of surface cross sections from the three sample types was obtained from metallographic sections taken near the apex of the C-rings. Near surface cross sections that are representative of the three sample

a

b

Figure 69. (a) Macrophoto of cracked C-ring S37, solution annealed starting condition, failed within 24 hours in a 3×10^{-2} Torr vacuum at 650°C . (b) SEM micrograph showing intergranular through crack in C-ring.

Figure 70. (a) Stereomicrograph showing dimpled surface of C-ring surface after shot peening. (b) SEM micrograph of shot peened surface at bend in C-ring S13 after 24 hours at 650°C in a 4×10^{-2} Torr vacuum.

types are shown in Figures 71a-c. As can be seen from Figures 71a and 71b, the solution annealed and stress relieved surfaces, respectively, appear similar. In cross section, the shot peened surface shows a deformed layer of material at the surface, as can be seen in Figures 71c and 71d. The shot peen size used in this experiment was 63 μm in diameter. The depth of the deformed layer at the surface of these samples was estimated from micrographs of surface cross sections to be 20 to 30 μm deep, approximately one third to one half the shot peen diameter. The maximum compressive stress that can be obtained by shot peening is approximately one-half the material's yield strength. [110] For alloy 908 in the solution annealed condition this value would be approximately -200 MPa.

Microhardness traces extending across the entire cross sections of these samples were also obtained and can be seen in Figures 72-74. As can be seen from Figure 72, the microhardness trace across a shot peened sample shows an increase in hardness in the deformed layer at the surface. The stress relieved sample's microhardness decreases at the surface, shown in Figure 73, and is consistent with stress relief occurring there. A material can be stress relieved by heating it to a temperature where the yield strength of the material is the same or less than the value of the residual stress. [114] For alloy 908 in the solution annealed condition, this value is approximately 400 MPa at 650°C. At this temperature the material can deform and relieve the stress through creep. It is important to note that the samples used in this study were cooled very slowly after the 650°C/16 hour stress relief heat treatment, and furnace cooling occurred under vacuum. Slow cooling is important so as not to reintroduce residual stresses. The microhardness trace across the solution annealed and failed sample is shown in Figure 74 and shows no change in subsurface hardness.

The results of the C-ring tests indicate that the elimination or reduction of the tensile residual stress component contributing to intergranular oxidation was responsible for preventing intergranular cracking. Another factor, that can contribute to these results may exist. Researchers have observed that changes in the surface stress state can alter the type of oxide formed. Shot peening produces Cr rich spinels versus (Fe,Ni)O type oxides. [40, 77, 78, 115] Improved oxidation resistance of shot peened materials has also been observed. [115] In the case of C-ring samples that had been used for metallographic preparation, and not preserved in a desiccator, rust (FeO) was found to have formed on the solution annealed and the stress relieved surfaces but not on the shot peened surface. To determine whether this was due to Cr enrichment, chemical analysis was conducted on oxides electrolytically extracted from the surfaces of the C-rings. Shot peened, stress relieved, failed solution annealed and intact solution annealed samples were analyzed. The results of this analysis are shown in the plot seen in Figure 75. Oxides from the two

Figure 71. Optical micrographs showing cross sections of the outer surfaces of C-ring test samples heat treated at 650°C for 24 hours in a 4×10^{-2} Torr vacuum. (a) Solution annealed sample S37, failed. (b) Vacuum heat treatment stress relieved sample S49, no failure. (c) Shot peened sample S13, no failure. (d) Higher magnification micrograph showing the 30 μm deep deformed layer caused by shot peening.

Figure 72. Microhardness profile across thickness of C-ring sample S13. Shot peened surface, heat treated at 650°C for 24 hours in a 10^{-2} Torr vacuum. No Failure. Trace runs from surface (0 μm) to inside diameter (3000 μm).

Figure 73. Microhardness profile across thickness of C-ring sample S49. Stress relieved sample, heat treated at 650°C for 24 hours in a 10^{-2} Torr vacuum. No Failure. Trace runs from surface (0 μm) to inside diameter (3000 μm).

Figure 74. Microhardness profile across thickness of C-ring sample S37. Solution annealed, heat treated at 650°C for 24 hours in a 10^{-2} Torr vacuum. Failure. Trace runs from surface (0 μm) to inside diameter (3000 μm).

Figure 75. Compositions of oxides (oxygen excluded from plot) electrolytically extracted from the surfaces of C-rings that were heat treated under degraded vacuum conditions (10^{-2} Torr range). SA = Solution Annealed, SR = Stress Relieved, and SP = Shot Peened.

longest time shot peened samples have high concentrations of Cr and Nb, with low concentrations of Fe and Ni. The short time, 24 hour, oxide sample shows a higher Fe concentration, with Cr and Nb levels low but above the matrix concentration. The trend of increasing Cr concentration for the shot peened samples corresponds to longer exposure times, allowing more of the Cr rich oxide to form. The oxide obtained from the failed solution annealed sample shows very high concentrations of Nb and of the easily oxidized hardening elements, Ti and Al. The concentration of Cr was well above the matrix concentration of 4 weight percent and exceeded that of the shot peened sample tested for an equivalent time. Interestingly, the solution annealed sample that did not fail shows a higher Cr concentration than the failed sample, but this may be due to a longer exposure time that allowed more of the oxide to form. The 24 hour stress relieved sample also showed a Cr concentration that was above that of the equivalent shot peened sample. It was initially thought that the stress relieved samples may have formed a Cr-rich oxide during their high vacuum heat treatment. And that this contributed to the fracture resistance seen in these samples. This supposition is not confirmed by these results. The observation that applies to all these samples is that Nb and Cr are present in the oxides. In the case of the shot peened samples, (Fe,Ni)O is present initially (24 hours) and the amount of Cr rich oxide increases with increasing exposure time. The high Cr concentration found in the shot peened oxides may account for their relative corrosion resistance when left exposed to air. Based on these chemical analyses, however, modification of surface stresses, either through shot peening or stress relief, are responsible for the lack of intergranular fracture in these samples. The oxide compositions of the stress modified samples at short times (24 hours) are not sufficiently enriched in Cr compared to the failed solution annealed sample to contribute to the results seen.

Examination of the fracture surfaces from the failed C-ring revealed fine structure in the SEM that was obscured by oxidation in the stress rupture samples. The SEM micrograph shown in Figure 76 is a composite across the wall thickness (ID to OD) of the failed C-ring sample S37. As seen in this micrograph, the intergranular fracture path extends through the full thickness of the sample, with only a thin, 50 μm , ductile layer at the inside surface, produced when the sample was broken open for examination. Higher magnification micrographs show the intergranular fracture surface to be brittle in character, with no evidence of ductility on the surfaces of the exposed grain boundaries, as shown in Figures 77a and 77b. Slip lines and twin boundaries can be seen very clearly on the grain surfaces in these micrographs. Their appearance is enhanced due their decoration by small white particles. At high magnification in the SEM, there was no variation in the density of these

Figure 76. SEM micrograph across intergranular crack in the C-ring S37 that failed within 24 hours at 650°C in a 4×10^{-2} Torr vacuum.

a

b

Figure 77. High magnification SEM micrographs taken near the inside diameter of the cracked cross section of C-ring S37 after failing within 24 hours at 650°C in a 4×10^{-2} Torr vacuum.

particles or fracture surface oxidation between the outside diameter and inside diameter of the sample. These particles and their association with slip lines in the material can be seen in Figures 78a. The high magnification micrograph seen in Figure 78b clearly shows the decoration of slip lines by these particles. One stage, extraction replicas were made from the fracture surface in an attempt to identify these particles. The polymeric film used for the extraction was carbon coated after being stripped from the fracture. SEM examination of the replica using EDS showed that no particles had been extracted from the surface, indicating that they were well bonded to the surface. Insitu EDS analyses showed oxygen present in the particles but the concentrations of the other elements were at matrix levels. This result suggests that the particles have compositions that contain the two major matrix elements, i.e., Ni and Fe, and have a stoichiometry close to the proportion of these elements in the matrix. C-ring experiments similar to these had been previously performed in commercial grade argon, and the fracture surfaces from these samples had shown fracture morphologies with similar decoration of slip lines as the degraded vacuum samples used in this study. The particles present on the argon tested samples, however, appeared to be coarser and hence easier to extract. SEM micrographs from the fracture surface of one of the C-ring samples that had been tested at 550°C for 200 hours in a commercial grade argon atmosphere ($O_2 \leq 5$ ppm) are shown in Figures 79a and 79b. Fracture characteristics already discussed for the degraded vacuum sample are apparent. White particles decorating the slip lines are coarser in this sample, as seen in Figure 80a, and may have coarsened during the longer 200 hour heat treatment and with a steady supply of oxygen from the argon gas. A one stage replica taken from the fracture showed the particles to be very adherent but a small number were extracted, some of which can be seen in Figure 80b. Semi-quantitative EDS analyses were obtained from 9 of the extracted particles. The resulting composition, in weight percent, was determined to be $38.7 \pm 5\%$ Fe, $39 \pm 5.8\%$ Ni, and $21 \pm 6\%$ O. To determine an approximate stoichiometry the atomic percent of these elements was $26 \pm 5\%$ Fe, $25 \pm 6\%$ Ni, and $47.7 \pm 9.9\%$ O, giving a compound with the formula (Ni,Fe)O. Interestingly this is the same oxide stoichiometry reported by Andrieu to be present in the intergranular cracking regime of alloy 718. [77, 78, 79] The SEM micrograph from a failed flat plate stress rupture is shown in Figure 80c as a comparison to the fractures seen in the C-ring samples. The region shown in this micrograph is associated with a grain that had fallen out during metallographic preparation. As can be seen inside the missing grain cavity, the grain boundaries are oxidized more heavily than the C-ring samples. The grain boundary oxide that can be seen in cross section

a

b

Figure 78. High magnification SEM micrographs taken along the cracked cross section of C-ring S37 after failing within 24 hours at 650°C in a 4×10^{-2} Torr vacuum. (a) Near inside diameter. (b) Near outside diameter.

a

b

Figure 79. High magnification SEM micrographs taken of the intergranular fracture surface from a cross section of the C-ring C33 after failing within 200 hours at 650°C in a commercial grade argon atmosphere.

Figure 80. (a) SEM micrograph taken from the intergranular fracture surface from a cross section of the C-ring C33 after failing within 200 hours at 650°C in a commercial grade argon atmosphere. (b) Oxide particles captured on an extraction replica of the C-ring fracture surface. (c) Comparable SEM micrograph from the flat plate stress rupture sample 49P (650°C/28.3 hours/1000 ppm oxygen) showing the oxidized character of the fracture surface at a pulled out grain boundary and the grain boundary oxide in cross-section.

as a gray border around the intact grain boundaries is similar to the oxide seen along the boundaries in the C-ring micrograph shown in Figure 80a.

V. DISCUSSION

This section is divided into two parts. The first part will discuss the stress rupture test results for alloy 908 and their implications for predicting safe heat treatment regimes for CICC magnets. Following it will be an analysis of the grain boundary oxygen embrittlement phenomenon based on experimental evidence obtained in this study. The results of this latter analysis will have more indirect but equally important consequences for CICC magnet heat treatment.

A. Stress Rupture Tests

For materials that exhibit some form of oxygen embrittlement, stress rupture data can be viewed from the perspective of a competition between the diffusion controlled processes of creep and intergranular embrittlement. Oxygen damage caused by intergranular oxidation, for example, can accelerate the creep rate and reduce ductility and life. This is because intergranular oxidation reduces the cross section over which the load is carried. [112] Similar observations were drawn from the alloy 908 stress rupture tests. When the creep rate was high, as it is at high temperatures and high loads, and the oxygen concentration low (< 1 ppm), creep rupture predominated over the entire sample cross section. If the creep rate was lowered by lowering temperature or load and the oxygen concentration increased, the intergranular oxidation rate overtook creep initially. Then, when the sample cross section decreased sufficiently, the creep rate increased with the increased cross sectional load. The result is a decrease in total rupture life when compared with a low oxygen concentration sample at the same temperature and load. The change in sample cross section, as indicated by the ratio of ductile fracture area to total fracture area, with increasing oxygen concentration, is shown in Figure 35.

Alloy 908 stress rupture data presented in Figures 20 and 21 show that the rupture times for the flat plate samples were relatively independent of oxygen concentration for low (≤ 1000 ppm) concentrations. The variation in rupture time with stress and temperature, however, was consistent with expected stress rupture behavior. Double notch round bar data shown in Figure 23 indicated that the rupture times for this sample geometry with 20% cold work are more sensitive to oxygen concentration. The long rupture time seen in the 3 ppm oxygen test for this sample geometry, however, precluded running additional tests to determine if this trend continued at lower (≤ 3 ppm) oxygen concentrations.

The fact that C-ring test samples fail within relatively short times and at relatively low oxygen concentrations questions the predictive ability of stress rupture testing (based on time to failure) for environmentally assisted phenomena. As seen in Figures 34 and 36 the establishment of a threshold oxygen concentration for oxygen assisted intergranular cracking based on percent intergranular fracture, with zero percent indicating that intergranular cracking will not occur, is a more appropriate way to utilize this data. A zero percent intergranular fracture criterion is based on two basic considerations that must be applied in order to select a safe oxygen threshold. First, even at low ($\leq 1\%$) percentages of intergranular fracture, intergranular cracking was stopped because failure by creep rupture prevented further intergranular damage. In other (actual) situations, intergranular oxidation and crack propagation will continue until the sample fails or the stresses driving it are relieved. Second, the oxygen threshold values that other researchers have reported for a range of nickel-iron based superalloys, stainless steels and other fcc metals generally fall within a fairly narrow range. These researchers have determined this threshold based on dynamic test methods. The value determined for alloy 908 based on percent intergranular fracture falls well within this range.

In order further evaluate the predictive ability of the stress rupture data for alloy 908 to the CICC magnet application, it is necessary to examine the data using a time-temperature parametric relationship.

The stress rupture data as presented in Figures 20 and 23, cover relatively small time, temperature, and stress regimes for a given oxygen concentration. In most cases, creep rupture data are presented using a time-temperature parameter that correlates time, temperature, and stress, allowing the data to be extrapolated. [110, 116, 117] One example of this is the extrapolation of stress rupture data to long times for components that will be in service for years or decades. Many time-temperature parameters have been developed to this end. [116, 117] The Larson-Miller parameter is the most commonly encountered of these. Since creep is a thermally activated process, the parameter was derived from the Arrhenius equation. The final form of the Larson-Miller relationship is expressed as

$$\frac{\Delta H}{R} = T(C + \log(t)) \quad (1)$$

where ΔH is the activation energy for creep, R is the gas constant, T is absolute temperature, t is time, and C is the material constant. In most cases the time is in hours.

For nickel-iron base superalloys the material constant C is assumed to be 20. A semilogarithmic plot of stress versus the Larson-Miller parameter, $T(C + \log t)$, using $C=20$ is shown in Figure 81 for flat plate samples tested in low oxygen, argon atmospheres.

Figure 81. Larson-Miller parameter plot for all flat plate test data, grouped by oxygen concentration with $C = 20$.

Because the alloy 908 flat plate stress rupture times were found to be relatively independent of oxygen concentration, the data in this plot have been grouped by oxygen concentration range. Branching or divergence can be seen in this plot for the 195 ppm oxygen range. Woodford examined divergence between air and argon (low ppm oxygen) stress rupture data and found it to be an environmental effect, related to the greater loss of sample cross section in air by oxidation. [118] For the flat plate samples, branching was found to be a function of stress, temperature, and oxygen concentration, and reflects an increase in rupture life with decreasing stress for a given test temperature and oxygen concentration. The 195 ppm oxygen data, for example, show divergence primarily because some of these data was generated at 750°C and, for a given stress, increasing the test temperature produces rapid failure with less intergranular fracture. This is the general result of decreased tensile strength and increased ductility with increased temperature that has been experimentally verified for alloy 908. [109] This is illustrated in the micrographs shown in Figures 33a-c for 750, 700 and 650°C tests at 650 MPa, respectively. The result is that the 750°C test samples fail in tension before the lower temperature samples and exhibit less intergranular fracture at comparable oxygen concentrations and stresses. This is apparent when comparing the times to rupture for the 650°C/650 MPa and 750°C/650 MPa data points in 195 ppm oxygen, 114.2 versus 0.06 hours, respectively, in Figure 22.

Flat plate air data for 5% cold work material from INCO are plotted along with the low ppm oxygen data in Figure 82. The position of the air data on the plot stems from rapid failure that is the result of a large loss (70-80% in round bar samples in air) in cross-sectional area due to intergranular oxidation. A similar plot for the round bar test data in air and at low oxygen concentrations is shown in Figure 83. This data shows better delineation with changing oxygen concentration. A transition in the round bar air data occurs between 200 and 300 MPa, at which air test samples can show rupture lives in excess of 1000 hours. The scatter in the rupture life in this range, however, is extreme, with some failures occurring in less than 1 hour for stresses below 300 MPa.[37] More test data in excess of 1000 hours would be required to verify this transition.

Data from both sample types and all test conditions are shown in Figure 84. In this plot the curves for both the air and low ppm oxygen in argon tests have been extrapolated to higher time-temperature parameters. A horizontal bar marks the ultimate tensile stress for alloy 908 at 650°C (586 MPa for 980°C/1 hour solution anneal). [109] The stresses sustained by the test samples are higher because notched samples can withstand higher stresses due to constraint against plastic flow. [113] Also, precipitation of the strengthening phase γ' occurs rapidly in this material, see Figure 19, producing an increase

Figure 82. Larson-Miller parameter plot of low oxygen concentration flat plate test data compared with 5% cold work flat plate test data from INCO. [105]

Figure 83. Larson-Miller parameter plot of round bar low oxygen concentration data for 20% cold work and solution annealed (SA, 980°C/1h) conditions compared with round bar data for 20% cold work material in air from Nicol. [37]

Figure 84. Larson-Miller parameter plot of combined round bar and flat plate test data. Time-temperature-stress lines have been extrapolated based on data shown. SA=Solution Anneal (980°C/1h) and CW = Cold Work. Air data Nicol [37], INCO [105]

in tensile strength. The region between 300 and 222 MPa marks the 650°C air transition regime for which the stresses are low enough to prevent rupture within 1000 hours. The two unfailed 1000 and 1200 hour air tests shown on the plot define this region. The right side of the plot is defined by the 0.01-1 ppm oxygen line, the labeled data points to the right of this line either did not fail or exhibited no intergranular cracking. The percentage intergranular fracture increases to the left of this line with increasing oxygen concentration. This plot could be used for extrapolation to CICC heat treatment conditions. The time-temperature parameter for 650°C/200 hour Nb₃Sn heat treatment, for example, would be 20.6×10^3 k-h and the stress at which rupture would occur is 604 MPa in a 0.01-1 ppm oxygen atmosphere, indicated by the vertical line in the plot. Alternately, in a 195 ppm oxygen atmosphere rupture would occur in 200 hours at 510 MPa. A magnet given a 550°C/200 hour Sn diffusion heat treatment would not fail in a 0.01-1 ppm oxygen atmosphere up to the ultimate strength at that temperature, or in air up to the 300 MPa transition stress. While this observation may be true on the basis of time to rupture, in actuality some intergranular cracking may have occurred before final failure.

One problem with the presentation of published stress rupture data is that the mode of failure (transgranular versus intergranular) is not always given. In many cases, fractographic examination of the samples has not been performed. In air tests of nickel and nickel-iron base superalloys, intergranular crack propagation due to oxygen may account for most of the time to rupture, with final transgranular rupture occurring rapidly in the remaining cross section area. [70, 71] In Figure 85 the data that were shown in Figure 81 have been replotted and in the legend labeled to show percent intergranular fracture. Comparing these plots, a transition in the 700 and 650°C data can be seen that corresponds to the decrease in percent intergranular fracture along the 0.01-1 ppm oxygen concentration line. For these temperatures, tests performed to the right of the sloped 0.01-1 ppm oxygen line will exhibit predominantly ductile transgranular fracture. Increasing the oxygen concentration moves the time-temperature parameter to the left of this line, and samples tested there will show an increased percentage intergranular fracture.

As discussed above, oxygen's most immediate effect on stress rupture data is to reduce the effective cross sectional area through intergranular oxidation. Woodford has suggested that the departure between air and argon data may be accounted for by correcting the Larson-Miller material constant, C , for loss of sample cross-section due to oxidation. [118] The alloy 908 data were examined using the graphical creep-rupture correlation that uses the convergence of isostress lines on a plot of $\log(t)$ versus $1/T$ to determine a value for the material constant C , where the equation for the isostress line is given by

Figure 85. Larson-Miller parameter plot of flat plate test data at low oxygen concentrations grouped by percent intergranular fracture.

$$\log(t) = -T + \frac{\text{constant}}{T} \quad [110, 117] \quad (2)$$

A value for the material constant C based on oxygen concentration could not be directly determined from the data. This was primarily because there was no correlation between time to rupture and oxygen concentration for the flat plate test samples. It was found, however, that if each set of stress-temperature data was grouped by percent intergranular fracture, a correlation did exist. The rationale behind this approach assumes that, for notched stress rupture samples, the time to rupture is close to the time to initiate a crack. [55] This assumption has been validated for both round bar and flat plate samples of alloy 908 tested in air by Nicol and Sizek, respectively. [37, 105] Also, if the data are grouped by percent intergranular fracture, it can be assumed that, for the same load and temperature, the stress on the remaining ductile area at failure was equivalent.

The data groupings for the 650 and 540 MPa isostress lines and their least squares fits are shown in Figure 86. In the plot seen in Figure 87, the 650 MPa data groupings have been consolidated and isostress lines drawn by least squares fits to the data. The average of the intercepts for the two isostress lines was used to obtain a value of 30 for the material constant C. The low ppm oxygen flat plate data were replotted using the new Larson-Miller parameter $T(30+\log t)$, and are shown in Figure 88. Comparison with Figure 81 shows the improved data fit using $C = 30$. By entering a time and temperature into the Larson-Miller parameter, the rupture stress can be read from the “master curve” shown in Figure 88. Alternately, if the stress and temperature are known, a time to rupture can be calculated. The time to rupture values obtained using $C = 30$ show good correspondence to the experimental values for the flat plate samples. The time to rupture for flat plate samples at 650°C and 650 MPa, for example, is predicted to be 117 hours from the curve. From the experiments, the mean time to rupture at 650°C is 108.3 ± 36 hours at 651 ± 18 MPa. In using this “master curve” it must be noted that it is applicable only to the midsection (0.1-1000 ppm oxygen) of the sigmoidal curve shown in Figure 36. In the plateau below 0.1 ppm oxygen, environmental effects are absent and pure creep rupture is controlling. The second plateau, above 1000 ppm oxygen, represents the regime where the rupture life is primarily controlled by a reduction in sample cross section (70-80%) due to intergranular oxidation.

Figure 86. Plot of isostress lines and least squares fits for 650 and 540 MPa stresses. Least squares fits for 650 MPa data have been grouped by percent intergranular fracture.

Figure 87. Plot of isostress lines and least squares fit for 650 and 540 Mpa stresses. The data for the 650 Mpa line are grouped by time to failure based on percent intergranular fracture.

Figure 88. "Master curve" for solution annealed flat plate stress rupture data based on new material constant $C = 30$.

B. Grain Boundary Analysis

The factors affecting the transition between internal/intergranular oxidation and external oxidation are the oxygen partial pressure and the concentration of the oxidizable solute. In Ni-Cr alloys and Ni-Fe base superalloys the external, passivating, oxide is either Cr_2O_3 or NiCr_2O_4 (these concepts were discussed in section F of the Literature Review). This transition in mode of oxidation appears correlate with the oxygen concentration dependence observed for intergranular oxidation in alloy 908. Of particular significance is the existence of a transition time to achieve a given depth of internal/intergranular oxidation. In matrix internal oxidation this time is linked to the nucleation and growth of oxide particles within the internal oxide zone. As the oxide particles in this zone coarsen, they act to block the diffusion paths for oxygen into the alloy. [82, 85] Oxygen diffusion into the alloy is effectively shut off once these oxide particles reach some critical volume fraction. [82, 85] The time required to reach this critical volume fraction determines the depth of internal oxidation. In an analogous manner, this work suggests that intergranular oxidation occurs within a subsurface zone. The depth of this zone is controlled by the oxygen concentration at the surface of the alloy. As with internal oxidation, the formation of intergranular oxides is required to block the intergranular diffusion of oxygen. As was discussed, the intergranular oxide formed in Ni-high Cr alloys is typically Cr_2O_3 . [96] Dilute (1-5 wt.% Cr) Ni-Cr alloys form varying proportions of Cr_2O_3 and NiCr_2O_4 intergranularly. [94] The predominant intergranular oxide deeper within the zone of internal/intergranular oxidation is Cr_2O_3 . [94]

The above observations explain why Cr was present in the intergranular oxide at the terminus of oxidized grain boundaries in the long-time flat plate samples. The round bar test samples formed only (Ni,Fe)-type intergranular oxides. These samples failed in too short a time to develop Cr-rich intergranular oxides. This is based on the internal oxidation model for the time required to form an oxide that can effectively block oxygen diffusion. An added factor in alloy 908 is the formation of oxides of Nb. In alloy 718, Gao reported that formation of intergranular Nb_2O_5 films may contribute to environmentally enhanced intergranular fatigue crack growth. [56] The oxides of niobium are thermodynamically stable at low partial pressures of oxygen, lower than Cr_2O_3 in fact. Unlike Cr-rich oxides, Nb oxides are non-protective, i.e., non-passivating.

Table 6 summarizes the compositions of surface and intergranular oxides obtained by EDS in the SEM for some of the stress-rupture samples. It should be noted that the oxygen potentials at the sample surface for all the tests done in this study are above the oxygen potentials for formation of most of the metallic oxides at 650°C, based on the Ellingham

Table 6. Compositions of Surface and Grain Boundary Oxides From Alloy 908 Stress Rupture Samples.

Oxide Location	Sample Type	Sample	O ₂ Potential (kcal/mole)	Time (h)	T (°C)	Composition (weight percent)*									
						Ni	Fe	Cr	Nb	Ti	Al	Si			
	Heat	Y9401K				49.3	40.8	3.99	3.04	1.55	1.01	0.16			
Surface	Flat	38P	-26.6	522	650	9.8	8.7	11.2	17.7	5.2	4.2	2.9			
Surface	Flat	8P	-25.5	211	650	16.9	20.8	15.2	6.7	7.0	3.3	1.7			
Surface	Flat	66T	-22.0	61.5	650	2.0	2.4	1.6	46.7	0.7	-	-			
Surface	Flat	62P	-18.67	122	650	24.0	28.0	5.9	6.1	3.6	1.4	-			
Surface	Flat	23P	-12.7	77	650	9.2	31.3	9.2	2.0	1.6	3.1	3.3			
Grain Boundary	Flat	62P	-18.7	122	650	37.2±7.7	37.5±5.1	7.8±2.9	4.8±2.9	1.9±0.4	1.3±0.2	0.4±0.1			
		Matrix				47.2±0.6	40.8±0.7	4.8±0.2	4.0±0.1	1.6±0.1	1.2±0.1	0.3±0.1			
Grain Boundary	Flat	49P	-12.7	28.3	650	45.6±8.0	27.2±6.9	8.1±4.0	5.9±1.2	2.6±0.1	1.8±0.4	0.6±0.2			
		Matrix				46.4±0.3	41.3±0.2	4.7±0.3	4.2±0.3	1.7±0.2	1.3±0.1	0.4±0.1			
Grain Boundary	Round	20cw31	-12.7	7.3	650	40.2	46.5	5.1	3.0	1.5	1.6	-			
		Matrix				46.3±0.9	41.2±1.0	4.7±0.3	4.6±0.4	1.9±0.2	1.2±0.1	-			
(Nb,Ti)C	Round	10cw2	-12.7	8.2	650	39.8	26.3	4.4	16.4	2.4	1	-			
Grain Boundary	Round	10cw2	-12.7	8.2	650	40.6	39.1	4.5	4.4	1.9	1.3	-			
		Matrix				41.1±0.7	46.9±0.8	4.7±0.3	4.2±0.4	1.8±0.3	1.2±0.3	-			
Grain Boundary	Round	1A	-12.7	12.3	650	40	38	4.6	4.3	1.6	1.4	-			
		Matrix				46±0.4	42±0.6	4.5±0.6	4.2±0.6	2.1±0.6	1.3±0.2	-			
Grain Boundary	Round	1B	-12.7	4.0	650	41.3	39.2	4.8	3.2	1.2	0.8	-			
		Matrix				46.1±0.3	42.2±0.5	4.6±0.1	4.2±0.4	1.8±0.2	1.1±0.2				
Grain Boundary	Flat	21P	-17.4	2.4	750	70.4±3.6	24.1±4.0	2.7±0.5	1.1±0.3	0.8±0.2	-	-			

*Balance Oxygen in Oxide Analyses

diagram. [119] The reported oxygen potentials, however, do not indicate the oxygen potential below the surface oxide layer or along the grain boundaries. At these locations the oxygen potential is determined by the kinetics of oxygen diffusion through the external scale and along the grain boundaries. [86]

When comparing these compositions it must be remembered that these were *in situ* analyses taken from metallographic cross sections and should be compared on a relative basis to the material heat composition also shown in the table. This is because these analyses incorporate some of the matrix elements due to subsurface scattering of the SEM electron beam during EDS. From the surface oxide analyses shown in this table, it can be seen that the low oxygen potential test samples above -12.7 kcal/mole (650°C, 1000 ppm oxygen) were enriched with respect to Nb and Cr. Enrichment in the other thermodynamically stable elements (Al, Ti, and Si) can also be seen in some of these samples. The sample tested at an oxygen potential of -12.7 kcal/mole shows enrichment of Cr but not Nb.

The grain boundary oxide EDS compositions are shown along with their corresponding matrix EDS compositions in Table 6. As seen in this table, the grain boundary oxide formed in the -18.7 kcal/mole oxygen potential (650°C, 38 ppm oxygen) flat plate sample is enriched in Cr, relative to the matrix. When comparing the matrix and grain boundary compositions, the elements Ni and Fe will appear diluted compared to their matrix compositions. This is because, by combining with oxygen to form oxides, the relative weight percents of these elements at the grain boundaries has decreased. The higher oxygen potential sample, -12.7 kcal/mole, is somewhat enriched in Cr and Ti, but also contains a high Ni content, indicating that the oxide contains a combination of Ni, Cr and Ti. In contrast, the intergranular oxides found in the round bar samples, show no enrichment of Cr relative to the matrix composition. This is in agreement with the EDS x-ray analyses shown in Figures 53, 54, 56, 58, 59, and 68 for the round bar test samples. This difference between the two sample geometries may not be related to oxygen concentration. Comparison of equivalent oxygen potentials, -12.7 kcal/mole, still shows more Cr in the flat plate sample. It is more likely that the longer life of the flat plate sample, 28.3 hours versus that of the round bars, allowed Cr_2O_3 , NiCr_2O_4 and/or $\text{Ni}(\text{FeCr})_2\text{O}_4$ to form on the grain boundary. This same time dependency was seen in the C-ring samples as presented in the Results section. The presence of an oxidized primary (Nb,Ti)C carbide, at the grain boundary in the round bar sample 10cw2, can be seen in Table 6. The Nb, and, to a lesser extent, Ti enrichment in this analysis, along with the presence of oxygen, confirms this. The composition of the intergranular oxide found in a 750°C flat plate sample is also shown in Table 6. At this temperature and oxygen potential (195 ppm

oxygen), this sample shows predominately Ni enrichment, indicating the formation of a Ni-rich oxide such as NiO under these test conditions.

Figures 41 through 44, in the Results section, demonstrate the presence of Nb-rich intergranular oxides in alloy 908 after testing. Those results were similar to the results reported by Gao for alloy 718. [56] The sample that was examined, 38P, also showed Nb enrichment of its surface oxide, as shown in Table 6. This sample did not, however, fail. Oxidation of primary (Nb,Ti)C carbides has been observed in many superalloys. [55, 56] This study also identified oxidation of (Nb,Ti)C as occurring in alloy 908, as was illustrated in the EDS x-ray map shown in Figure 54. Bricknell and Woodford identified niobium as one of the primary constituents of the internal and grain boundary oxides found in alloy 903A (commercial designation 907). [28] Analysis for oxygen was not included in their study, allowing for the possibility that the grain boundary phase may not have been an oxide. Niobium did not appear to play a role in the round bar test results. These samples, as seen in Table 6, did not show Nb enrichment of the intergranular oxides. It is evident, however, that (Ni,Fe)O type oxides were present at the grains boundaries in these samples.

As was shown in Figures 46 and 47, for an interrupted flat plate test, the intergranular fracture surfaces were oxidized up to the intergranular-transgranular transition. No zone of embrittled, oxide free grain boundaries could be found beyond the existing oxidized crack. This observation indicates that the grain boundaries ahead of the crack are not inherently embrittled by oxygen and that grain boundary oxidation is a required part of the crack growth mechanism. The lack of long range oxygen embrittlement observed in alloy 908 is consistent with that from fatigue crack growth studies in other materials. In these studies, when fatigue specimens are tested sequentially in air then in vacuum the crack growth rate drops from the high rate in air as soon as vacuum is reestablished. [41, 42, 43, 53, 120] In the fatigue crack growth situation this indicates that the crack growth rates are dependent only upon the existing environment. Also the effect is limited to the crack tip region and is not dependent upon the long range diffusion and embrittlement by oxygen of grain boundaries ahead of the crack. [53, 57]

Unstressed samples, tested along with their stressed counterparts, did not show any signs of intergranular embrittlement when fractured after testing at 650 and 700°C. Tensile samples that were placed, unloaded, in the same environment and then tested in air showed no change in properties when compared with tensile samples heat treated in vacuum (1×10^{-5} Torr) for similar times. The solution annealed (980°C/1 hour) samples exposed in the retort at 650°C for 188 hours in 35.5 ppm oxygen, along with stress rupture sample 60P, showed a yield strength of 1050 ± 70 MPa, ultimate strength of 1445 ± 7 MPa, and an elongation of $17.5 \pm 0.7\%$. This compares with a yield strength of 1075 MPa, ultimate

strength of 1433 MPa, and an elongation of 15.5% for solution annealed alloy 908 heat treated at 650°C for 200 hours in vacuum. [109]

An activation energy for intergranular oxidation in air was calculated for alloy 908. This calculation was based on measurements of intergranular oxidation depth obtained from round bar test samples used in a prior study. [37] If it is assumed that the depth of oxidation increases parabolically with time then,

$$x^2 = Kt \quad (3)$$

where x is distance, t time and K is a kinetic factor that includes the diffusion coefficient of oxygen. [98, 112, 121] The Arrhenius equation for K , where Q_{gb} is the activation energy for intergranular oxidation, is given by

$$K = K_o \exp\left(\frac{-Q_{gb}}{RT}\right) \quad (4)$$

Combining the two equations and rearranging gives

$$\log\left(\frac{x^2}{t}\right) = \log K_o - \left(\frac{Q_{gb}}{2.3 R}\right) \frac{1}{T} \quad (5)$$

where the slope of an Arrhenius plot, $\log x^2/t$ versus $1/T$, gives a value for Q_{gb} . A plot for the alloy 908 air stress rupture data is shown in Figure 89.

An intergranular activation energy, Q_{gb} , of 202 kJ/mole (48.2 kcal/mole) in air, was calculated from this plot. The value of 908 can be compared with air Q_{gb} values of 280 kJ/mole for Rene'80 by Chang, 274 kJ/mole for Ni 270 by Iacocca, 287 kJ/mole in alloy 718 by Gao, and 335 kJ/mole for a 20Cr-25Ni-Nb stainless steel obtained by Emsley. [56, 61, 98, 121] The lower activation energy obtained for alloy 908 is related to the greater susceptibility of this material to intergranular oxidation in air. The times used for the air samples were relatively accurate, given that the time for intergranular crack growth was very rapid and accounted for most of the sample life. [37] A similar analysis for the low oxygen concentration flat plate samples was also carried out. The Q_{gb} was calculated to be 492 kJ/mole (118 kcal/mole) in 195 ppm oxygen. The Arrhenius plot used for this calculation is shown in Figure 90. A Q_{gb} of 537 kJ/mole (128 kcal/mole) was determined for all the flat plate samples in the 38-195 ppm oxygen range, and this plot is shown in Figure 91. These high values reflect a number of factors. One is that the activation energy for intergranular oxidation at low oxygen concentrations is higher. This is reflected in the longer times required to achieve a given depth of internal/intergranular oxidation as the oxygen concentration is decreased. The other main factor is related to the flat plate test samples themselves. As was discussed in the Results section, the time to failure in these samples was relatively independent of oxygen concentration. This was related to a sample geometry that produced a plane stress state at the notch that results in less constraint against

Figure 89. Arrhenius activation energy, Q_{gb} plot for intergranular oxidation in alloy 908 in air. Based on round bar stress rupture data. $Q_{gb} = 202$ kJ/mole (48.2 kcal/mole).

Figure 90. Arrhenius activation energy, Q_{gb} plot for intergranular oxidation in alloy 908 in 195 ppm oxygen. Based on flat plate stress rupture data. $Q_{\text{gb}} = 492 \text{ kJ/mole}$ (118 kcal/mole).

Figure 91. Arrhenius activation energy, Q_g plot for intergranular oxidation in alloy 908 in 38-195 ppm oxygen. Based on flat plate stress rupture data. $Q_g = 537$ kJ/mole (128 kcal/mole).

plastic flow at the notch than in the triaxial stress state at the circumferential notch round in bar samples. [122] Because the flat plate rupture times were relatively constant for all oxygen concentrations the time component in the Arrhenius plots may not reflect the actual time for intergranular oxidation to occur. The time may instead be a combination of intergranular oxidation and plastic flow by creep. The depth of intergranular oxidation component, x , is accurate and is related to the oxygen concentration present. This is seen in the percent intergranular fracture versus oxygen concentration relationship that was shown in Figure 34. A plot for the flat plate test data in the 6 to 1000 ppm range is shown in Figure 92. In this plot the test data at each temperature has been combined and the scatter shown. The scatter in the 650°C data illustrates the change in depth of intergranular oxidation, x , with changes in oxygen concentration. A Q_{gb} of 508 kJ/mole (121 kcal/mole) was calculated from this plot and falls between the two other oxygen ranges reported for the flat plate samples.

C. C-Ring Tests and Modification of Residual Stresses

From the standpoint of simulating the residual stresses present in post fabrication conduits, the C-ring test results have more applicability. Altering the residual stress state at the surface of alloy 908 can prevent intergranular cracking in alloy 908. The effect of shot peening and stress relief are promising, although it is not clear whether this is simply a mechanical effect or has an effect on oxidation. Skelton and Bucklow observed that the oxidation rate of a low alloy steel increased due to surface working. [52] They ranked oxidation rates as surface worked < annealed < internally strained. Bainitic samples that were internally strained and then had their internal strains relieved by tempering showed oxidation rates comparable to annealed samples. [52] Surface deformation was reported to enhance Cr_2O_3 formation in Ni-Cr alloys containing between 10 and 30 wt.% Cr. [116] Giggins, et al., attributed this to the fine grain size produced by recrystallization of deformed surface layers at 900 and 1100°C. [116] Reports of enhanced Cr-rich oxide formation that occurs in superalloys and stainless steels after shot peening appear to support this conclusion. [77, 115] A similar enrichment in Cr was found in the long time shot peened alloy 908 C-ring samples. In this case, however, an association between improved SAGBO resistance and the presence of a Cr-rich oxide layer could not be demonstrated. This is because the beneficial effect of shot peening came in the short term (24 hour tests), where no substantial Cr enrichment was observed. Solution annealed samples that did not fail, and were tested for long times (200 hours) showed similar increases in Cr concentration in their surface oxides. It is apparent from these results that

Figure 92. Arrhenius activation energy, Q_{gb} plot for intergranular oxidation in alloy 908 in 6-1000 ppm oxygen. Based on flat plate stress rupture data. $Q_{\text{gb}} = 508$ kJ/mole (121 kcal/mole).

shot peening, or stress relief, act to mechanically alter the surface residual stress state. This was of particular benefit to SAGBO prevention because these methods suppress cracking during short times, before a sufficiently developed Cr-rich passivating surface oxide can form to protect the material. The deformed surface layer in the shot peened samples did not recrystallize at 650°C. Niobium enrichment was not detected in the intergranular oxides found on the C-ring fracture surfaces. It's presence in the surface oxide may indicate that a porous, non-passivating oxide formed, and that it was not a sufficient barrier to oxygen diffusion to prevent intergranular oxidation and cracking.

Andrieu and Pineau's oxidation cracking mechanism also has application to the results of this study, in particular, the increase in the chromium concentration as the C-ring test time increased. [40, 78] In short time tests, 24 hours, (Ni,Fe)O oxide was shown to be present on the C-ring fracture surfaces. Based on their kinetic argument, the long time samples show Cr enrichment, and had reached the transition time, t_p , required to nucleate and grow Cr-rich oxides. The short time samples were below the transition time for Cr-rich oxide formation, formed (Ni,Fe)O intergranular oxides, and cracked faster than the rate of Cr passivation.

D. Analysis of Stress Accelerated Grain Boundary Oxidation

It is proposed that stress accelerated grain boundary oxidation can be modeled as an internal oxidation process. The basis for this proposal was introduced in section F of the Literature Review. In stress accelerated grain boundary oxidation, low temperatures ($<1000^{\circ}\text{C}$) and application of tensile stress, favor grain boundary diffusion over lattice diffusion. The result is internal/intergranular oxidation that follows the internal/matrix oxidation model. The assumptions that serve as the basis of this proposed mechanism are:

- Intergranular oxidation in stress rupture samples continues until the sample fails, i.e., until final fast ductile fracture. This was demonstrated in this thesis.
- At low temperatures, and under an applied tensile stress, grain boundary diffusion is dominant ($D_{\text{lattice}} \lll D_{\text{gb}}$). The fact that non-stressed material used in these experiments did not exhibit intergranular oxidation supports the necessity of tensile stresses to further enhance intergranular oxidation.
- The “internal oxidation zone” at low temperatures and under tensile stress manifests itself as intergranular oxidation.
- The intergranular oxidation zone penetrates to the same depth as predicted for internal oxidation. Because $D_{\text{lattice}} \lll D_{\text{gb}}$, no internal (matrix) oxidation occurs.
- Analogous to internal (matrix) oxidation, the transition from internal to external oxidation is promoted by lowering the surface oxygen concentration and/or increasing the Cr concentration in the alloy.
- Also analogous to internal oxidation in Ni-Cr alloys, the nucleation and growth of intergranular Cr_2O_3 and NiCr_2O_4 precipitates serves to block the diffusion path for oxygen.
- The external oxide layer formed at the low oxygen concentrations (≤ 1000 ppm) used in these experiments was thin ($< 0.2\ \mu\text{m}$) or incomplete. Also, tensile loading will rupture this external oxide layer. Based on these observations, it can be assumed that diffusion through the external scale is not rate limiting. This allows the problem to be treated as internal oxidation in the absence of an external scale.

Definition of terms:

- $N_{Cr}^{(0)}$ is the mole fraction of chromium in the alloy.
- $N_O^{(S)}$ is the mole fraction of oxygen at the surface.
- N_O is the mole fraction oxygen in the base metal.
- N_{Cr} is the mole fraction of chromium.
- D_O is the diffusion coefficient for oxygen.
- D_{Cr} is the diffusion coefficient for chromium.
- D_{gb}^O is the grain boundary diffusion coefficient for oxygen.
- D_{gb}^{Cr} is the grain boundary diffusion coefficient for chromium.
- v is the stoichiometric ratio of oxygen to metal atoms in the oxide precipitate.
- ξ is the depth of the zone of internal oxidation.
- x is the distance from the outer surface.
- t is the reaction time required to form an internal oxide zone of depth ξ .
- γ is a time-independent dimensionless parameter, for isothermal oxidation at constant oxygen pressure.

The following derivation for the depth of internal oxidation follows that of Rapp. [82] Under diffusion control and in the absence of an external scale, the depth of the internal oxidation zone is a parabolic function of time, is given by,

$$\xi = 2\gamma(D_O t)^{1/2}. \quad [82] \quad (6)$$

Rapp has solved the one-dimensional diffusion equations for oxygen and for some oxidizable alloying element, in this case chromium. For oxygen,

$$\frac{\partial N_O}{\partial t} = D_O \frac{\partial^2 N_O}{\partial x^2} \quad (7)$$

the boundary conditions used are

$$\begin{aligned} N_O &= N_O^{(S)} & \text{for } x = 0, t > 0 \\ N_O &= 0 & \text{for } x \geq \xi, t > 0. \end{aligned}$$

For chromium the diffusion equation is,

$$\frac{\partial N_{Cr}}{\partial t} = D_{Cr} \frac{\partial^2 N_{Cr}}{\partial x^2} \quad (8)$$

and the boundary conditions applied are

$$N_{Cr} = N_{Cr}^{(o)} \quad \text{for } x > 0, t = 0$$

$$N_{Cr} = 0 \quad \text{for } x \leq \xi, t > 0.$$

The solutions obtained by Rapp are

$$N_O = N_O^{(s)} \left\{ 1 - \frac{\text{erfc}[x/2] (D_O t)^{1/2}}{\text{erf } \gamma} \right\} \quad (9)$$

$$N_{Cr} = N_{Cr}^{(o)} \left\{ 1 - \frac{\text{erfc}[x/2] (D_{Cr} t)^{1/2}}{\text{erf } \gamma \phi^{1/2}} \right\}. \quad (10)$$

In these equations $\phi = D_O/D_{Cr}$.

If an insoluble and stoichiometric oxide precipitates at the front of the zone of internal oxidation, the flux of oxygen atoms arriving from the surface must be equivalent to the flux of Cr arriving from the bulk alloy and,

$$\lim_{\epsilon \rightarrow 0} \left[-D_O \left(\frac{\partial N_O}{\partial x} \right)_{x=\xi-\epsilon} = -v D_{Cr} \left(\frac{\partial N_{Cr}}{\partial x} \right)_{x=\xi+\epsilon} \right]. \quad (11)$$

Substituting equations (9) and (10) into equation 11 gives

$$\frac{\partial N_O}{\partial t} = \frac{\exp(\gamma^2) \text{erf } \gamma}{\phi^{1/2} \exp(\gamma^2 \phi) \text{erfc}(\gamma \phi^{1/2})}. \quad (12)$$

Rapp obtained a solution for γ for the case where,

$$\frac{D_{Cr}}{D_O} \ll \frac{N_O^{(s)}}{N_{Cr}^{(o)}} \ll 1 \quad (13)$$

which is shown graphically in Figure 93. [82] This simplifies equation (12) to

$$\gamma \equiv \left[\frac{N_O^{(s)}}{2 v N_{Cr}^{(o)}} \right]^{1/2}. \quad (14)$$

Finally, substituting the expression for γ into equation (6) gives an expression for the depth of internal oxidation,

$$\xi \equiv \left[\frac{2 N_O^{(s)} D_O}{v N_{Cr}^{(o)}} t \right]^{1/2}. \quad (15)$$

The validity of the condition stated in equation 13 and illustrated in Figure 93 can be verified for the formation of an intergranular oxidation zone of depth ξ . The micrograph shown in Figure 94 is from a cross section near the surface of a heat treated alloy 905 sample, composition given in Table 1. This material has no Cr and low Al concentration. The intergranular and surface oxides that form in this material have been identified as

Figure 93. Concentration profile for the exclusive internal oxidations of alloys for the case where $\frac{D_{Cr}}{D_O} \ll \frac{N_O^{(s)}}{N_{Cr}^{(o)}} \ll 1$. From Rapp. [82]

Figure 94. SEM micrograph showing cross section through the oxidized surface of heat treated alloy 905.

Nb_2O_5 . [1] Extended time heat treatments rapidly overage the γ' (bct Ni_3Nb) precipitate in this material. [1] This rapid coarsening lends itself to using the γ' as a marker for niobium distribution using SEM. Coarse platelets of γ' can be seen in the lower portion of the micrograph and oxide precipitates can be seen along the grain boundaries. As the surface oxide develops, the intergranular oxidation zone extends into the alloy and the depletion of Nb from the matrix can be seen as a zone denuded of coarse γ' . As illustrated, the intergranular oxidation zone penetrates to the same depth as the solute depleted zone in this material. The data given in Table 2 provide another verification of the profile in Figure 93. From that data, at low temperatures ($< 800^\circ\text{C}$), the Cr concentration at the front of internal oxidation in Ni-Cr alloys does not drop off steeply.

For the conditions used in this thesis, the mole fraction of Cr, $N_{\text{Cr}}^{(o)}$, is fixed at 0.045. The concentration of oxygen at the surface of the stress rupture samples was measured. From Sievert's law $N_{\text{O}}^{(s)} \propto (P_{\text{O}_2})^{1/2}$. For Cr_2O_3 forming as an intergranular oxide $v = 3/2$. If grain boundary diffusion dominates under conditions at which stress accelerated grain boundary oxidation occurs, then equation (15) becomes

$$\xi \equiv [29.6 N_{\text{O}}^{(s)} D_{\text{gb}}^{\text{O}} t]^{1/2} \quad (16)$$

A value for the grain boundary diffusion of oxygen, D_{gb}^{O} , can be estimated for alloy 908 from

$$D_{\text{gb}} = 1.0 \exp\left(-9.35 \frac{T_{\text{m}}}{T}\right) \text{ cm}^2\text{s}^{-1} ; 1.0 < T_{\text{m}}/T < 2.4. \quad [89] \quad (17)$$

For alloy 908 at 650°C , $T_{\text{m}}/T = 1.77$, and $D_{\text{gb}} = 6.5 \times 10^{-8} \text{ cm}^2\text{s}^{-1}$. The depth of intergranular oxidation in the flat plate material was calculated as a function of surface oxygen concentration and experimental test time using equation (16). Intergranular oxidation depths for the round bar material were calculated using an analogous equation derived for cylindrical samples

$$\frac{(r_1)^2}{2} - (r_2)^2 \ln\left(\frac{r_1}{r_2}\right) + \frac{1}{2} = \frac{2N_{\text{O}}^{(s)} D_{\text{gb}}^{\text{O}} t}{v N_{\text{Cr}}^{(o)}} \quad (18)$$

where r_1 is the sample radius and r_2 is the un-oxidized core radius. [92] The values obtained were plotted with the experimental measurements of intergranular oxidation depth and are shown in Figure 95. The calculated values follow the trend of the experimental values. At low oxygen concentrations the depth of intergranular oxidation is at or near zero. This is the point at which the external/intergranular transition occurs. The depth of intergranular oxidation then increases as the concentration of oxygen at the surface

Figure 95. Comparison of experimental and calculated intergranular oxidation depths as a function of surface oxygen concentration at 650°C and 650 MPa. Based on experimental time to failure of stress rupture samples.

increases. The time to achieve the experimental intergranular oxidation depths of were calculated using equation (16). A plot of these data are shown in Figure 96. A line has been drawn on the plot to show the estimated oxygen concentration at which the transition from external to internal oxidation occurs. To the left of this line, $N_O^{(S)} D_{gb}^O \ll N_{Cr}^{(o)} D_{gb}^{Cr}$ and external oxidation is prevalent. [85] In this region, below approximately 1 ppm oxygen, $N_O^{(S)}$ controls oxidation. To the right of this line $N_{Cr}^{(o)}$ controls intergranular oxidation. Below 1 ppm oxygen the alloy passivates by external scale formation, in this analysis assumed to be Cr_2O_3 . Above 1000 ppm oxygen the assumption that an external oxide layer is not present is no longer valid and diffusion through the external oxide is rate limiting. Under these conditions the second plateau in the sigmoidal curve develops. In some cases the experimental times to the right of the line were somewhat longer than those calculated. In the stress rupture tests, intergranular oxidation proceeded to the depth predicted by internal oxidation theory. As was discussed earlier, ductile creep rupture of the remaining cross section contributed to the final failure times measured in these experiments. A schematic of the intergranular oxidation zone, of depth ξ , developed under tensile loading, is shown in Figure 97. Following internal oxidation theory, the intergranular oxidation zone stops at depth ξ after sufficient oxide (Cr_2O_3 or $NiCr_2O_4$) has precipitated to block further diffusion of oxygen. The time required to produce a 0.5 mm deep zone of intergranular oxidation in alloys 718, 908, and 903, as a function of oxygen concentration, are compared in Figure 98. As evident in this figure, increasing $N_{Cr}^{(o)}$ increases the time required to attain the same depth of intergranular oxidation. The higher activation energy calculated for intergranular oxidation at low oxygen concentrations is reflected in Figure 98. The time required to form a 0.5 mm zone of intergranular oxidation is longer at low oxygen concentrations than in air. This indicates that a greater barrier to intergranular oxidation exists under low oxygen conditions. As discussed above, the barrier to intergranular oxidation below 1 ppm oxygen is related to the transition from intergranular to external oxidation. A comparison of Figure 37 in the Results section, to Figure 98 shows why the percent intergranular fracture in alloy 908 lies above the alloy 718 data. It is expected that under equivalent loading conditions, alloy 908 will show greater a intergranular oxidation depth (and percent intergranular fracture) than alloy 718. Chromium plays an analogous role in stress corrosion cracking in aqueous systems. The data shown in Figure 99 are from a study on the effect of grain boundary Cr concentration on percent intergranular cracking in Ni-Cr-Fe alloys. [123] The data were obtained from constant extension rate tests (CERT) at room temperature in 0.017M $Na_2S_4O_6$. [123] As can be seen in this figure, there is a direct correlation between percent intergranular

Figure 96. Calculated time to reach depth of intergranular oxidation observed in stress rupture tests at 650°C and 650 MPa. Times for oxygen concentrations at or below 1 ppm are close to zero since no or small depths of intergranular oxidation were found below 1 ppm oxygen.

fracture (or depth of intergranular cracking) and the grain boundary Cr concentration.

Figure 97. Intergranular oxidation zone (of depth ξ) developed under tensile loading.

Translated to fatigue loading, for a fixed oxygen concentration, da/dN will be greater in the lower $N_{cr}^{(0)}$ alloys. This is because the depth of intergranular oxidation developed ahead of the crack tip will be greater. As the grain boundary area increases the effects of intergranular oxidation on da/dN should also increase. The increase in da/dN in alloy 718, under intergranular oxidation conditions, with decreasing grain size has been demonstrated in alloy 718. [47] Due to rupture of the external scale during crack advance the assumption that an external oxide is absent exists during fatigue loading.

Figure 98. Time to develop a 0.5 mm deep zone of internal oxidation in three alloys at 650°C as a function of oxygen concentration and mole fraction Cr.

Figure 99. Percent intergranular fracture as a function of grain boundary Cr level in Ni-Cr-Fe alloys obtained from constant extension rate tests at room temperature in 0.017M $\text{Na}_2\text{S}_4\text{O}_6$ (extension rate 2.5×10^{-5} mm/s). From Was [123].

VI. SUMMARY

At equivalent loads and oxygen concentrations, the round bar material failed in shorter times than the flat plate material. The intergranular oxide that formed was predominately (Ni,Fe)O type in the round bar material. Time to rupture in the flat plate material was independent of oxygen concentration over the 0.01-1000 ppm oxygen range examined. In this same geometry, the stress rupture test conditions provided a competition between creep rupture and loss of sample cross section due to intergranular oxidation. This observation corresponds to a creep damage mechanism based on loss of internal section by intergranular oxidation, following the methodology of Ashby and Dyson. [112] The intergranular oxides in these samples contained higher concentrations of Cr and Nb as based on EDS results. A strong correlation between oxygen concentration and percent intergranular fracture was observed and is similar to the results reported for alloy 718 under slow strain rate tensile loading. [77, 78] In each case, the percent intergranular fracture is related to the depth of intergranular oxidation that can occur under tensile loading at a given oxygen concentration. Based on percent intergranular fracture, a conservative value for the partial pressure of oxygen of 1×10^{-4} Torr is recommended for the heat treatment of alloy 908 under residual or applied stresses. Overall, with the exception of providing a threshold of oxygen concentration based on percent intergranular fracture, the stress rupture test results are more strongly dependent on the sample geometries and test method itself. It is not recommended that the time to failure generated by these tests be used to predict the expected heat treatment life at different oxygen partial pressures unless a clear understanding of the stress state in a fully wound Cable-In-Conduit-Conductor magnet is developed.

Based on the results of this study intergranular oxidation precedes cracking. Crack advance occurs after the intergranular oxide cracks in tension. All the materials examined in this study failed by stress assisted intergranular oxidation. The grain boundaries associated with intergranular fracture, either in the stress rupture samples or C-ring samples, were oxidized. This was also the case for grain boundaries found at intact notches in failed round bar samples. Even fracture surfaces that did not have a continuous oxide film coverage, in C-ring samples, showed signs of oxide precipitation on slip planes of the intergranularly fractured grain surfaces. The oxides formed at the grain boundaries were predominantly of the (Fe,Ni)O type. High temperature oxidation research on Ni-Fe base superalloys has shown these oxides to be permeable to oxygen.

The role of tensile stress, as suggested by intergranular oxidation studies, may simply be to accommodate the volumetric expansion that occurs as the intergranular oxides form.

In Cr-containing alloys, the kinetics of the intergranular oxidation mechanism are especially important. The depth of the intergranular oxidation zone that develops in an alloy is dependent upon both the oxygen partial pressure at the surface of the sample and the Cr content of the alloy. Whether a transformation from internal to external (surface passivation) oxidation occurs is also dependent on these two parameters.

In alloy 908, the amount Cr incorporated into the intergranular and surface oxides increases with increasing stress rupture life. The measured intergranular oxidation depths in alloy 908 were calculated using an analysis approach developed for internal oxidation. Agreement between the experimental and calculated depths, as a function of oxygen concentration, was verified. Based on this analysis, the time required to reach a given depth of intergranular oxidation is dependent upon the growth of Cr-rich oxides. Analogous to internal oxidation, these oxides act to block oxygen diffusion. The formation of these oxides is controlled by chromium grain boundary diffusion and the weight percent Cr in the alloy. The weight percent Cr dependency observed in high temperature intergranular oxidation follows that observed for intergranular stress corrosion cracking in aqueous environments.

The results found in this study can be related to the role of Nb-rich intergranular phases in reducing stress accelerated grain boundary oxidation in low-Cr or Cr free alloys. As these phases grow during heat treatment they act as intergranular barriers to oxygen diffusion. Alternately, by oxidizing, these phases can also act as oxygen traps. This was as was observed for primary (Nb,Ti)C carbides that oxidized in alloy 908.

Based on this study and a literature review of a wide variety of Ni and Ni-Fe base superalloys, if stresses can not be controlled, then heat treatment should occur in a 1×10^{-4} Torr or better vacuum for reliable protection against SAGBO. Modification of surface residual stresses through shot peening appears to be a relatively simple solution to the SAGBO problem. Stress relief in vacuum is less of an alternative because it requires that a high vacuum furnace vacuum be used. This solution does, however, suggest that leaks that develop in a vacuum furnace after a stress relief period may be of little consequence.

Some solutions to the stress assisted intergranular oxidation cracking seen in low coefficient of expansion superalloys in order of practical application to Cable-In-Conduit-Conductor magnets are;

- Place the surface of the conduit in compression,
- Keep the oxygen partial pressure below 1×10^{-4} Torr,
- Eliminate residual stresses by stress relief,
- Introduce localized Cr enrichment, either through plating or ion implantation of Cr,

- Add oxygen getter elements that segregate to grain boundaries (B, Zr, etc.).

VII. CONCLUSIONS

Applied

- Control of furnace atmosphere chemistry during heat treatment is essential for the successful heat treatment of alloy 908.
- An oxygen partial pressure below 1×10^{-4} Torr is required to successfully heat treat an alloy 908 Cable-In-Conduit-Conductor magnet.
- For stress rupture testing of low coefficient of expansion superalloys, an oxygen concentration threshold based on zero percent intergranular fracture is a better indicator of the potential for intergranular fracture during heat treatment than one based on time to rupture.
- The elimination of residual tensile surface stresses by applying compressive residual stresses through shot peening or reduction in tensile stresses through vacuum stress relief heat treatments eliminates stress accelerated grain boundary oxidation in C-ring bend samples.

Stress Accelerated Grain Boundary Oxidation

- The mechanism for high temperature intergranular fracture in alloy 908 is stress assisted intergranular oxidation cracking.
- The percent intergranular fracture in alloy 908 increases with increasing oxygen concentration.
- This result can be correlated to that observed in other Ni-Fe and Ni base superalloys and is controlled both by the concentration of oxygen in the environment and the concentration of Cr in the alloy.
- Long range, intergranular oxygen embrittlement was not observed in alloy 908.
- The fact that non-stressed material used in these experiments did not exhibit intergranular oxidation supports the proposal that tensile stresses enhance intergranular oxidation.

- The concentration of Cr incorporated into intergranular and surface oxides increases with increasing test duration. These results are consistent with internal oxidation theory.
- Internal oxidation, at low temperatures ($< 800^{\circ}\text{C}$) and under an applied tensile stress manifests itself as intergranular oxidation in alloy 908.
- The intergranular oxidation zone penetrates to the same depth as calculated for internal oxidation with $D = D_{gb}^0$. Because $D_{\text{lattice}} \lll D_{gb}^0$, no internal (matrix) oxidation occurs.
- Analogous to internal (matrix) oxidation, the transition from internal to external oxidation is promoted by lowering the surface oxygen concentration and/or increasing the Cr concentration in the alloy.
- Also analogous to internal oxidation in Ni-Cr alloys, the nucleation and growth of intergranular Cr_2O_3 and NiCr_2O_4 precipitates serves to block the diffusion path for oxygen.
- High temperature, stress assisted intergranular oxidation cracking is prevalent in most Ni-Fe and Ni base superalloys. Its effect diminishes with increasing Cr concentration.
- This failure mechanism's dependence on chromium concentration is similar to that observed for intergranular stress corrosion cracking in aqueous environments.

VIII. FUTURE WORK

The flat plate test samples offer little in the way of predictive ability as related to SAGBO. Further work should continue with the round bar configuration, but only to establish a fundamental data base for thick wall extruded conduit designs.

Most data reported in the literature is from fatigue and creep crack growth studies. Fatigue experiments are not directly applicable to the Cable-In-Conduit-Conductor situation; one cycle consisting of heat treatment, and creep crack growth studies may be preferable. If fatigue crack growth rate studies are carried out, they must be done under controlled oxygen partial pressures, low (< 0.05 Hz) frequency, and the effect of hold time should be investigated.

It should also be investigated if the low coefficient of expansion of these superalloys contributes to their susceptibility to stress assisted oxidation by preventing relaxation of stresses at the crack tip through thermal expansion. This is because, under static loading, the growing intergranular oxide can generate a stress field on the grain boundary ahead of the crack that allows further oxidation and crack advance.

Finally, the effect of tensile stress on the grain boundary diffusion coefficient for oxygen should be determined. Using internal oxidation methodology, an activation energy for grain boundary oxygen diffusion could be calculated from the depths of intergranular oxidation as a function of stress and temperature. This experiment would have to employ a constant stress test procedure.

APPENDIX

Table 1A. Nominal Compositions of Some Superalloys

Alloy	Composition (weight percent)										
	Fe	Cr	Ni	Co	Nb	Ti	Al	Mo	W	C	Si
617	—	22.0	54	12.5	—	—	1.0	9.0	—	0.07	—
Waspaloy	—	19.5	58.0	13.5	—	3.0	1.3	4.3	—	0.08	—
Astroloy	—	15.0	55.0	17.0	—	3.5	4.0	5.3	—	0.06	—
MAR-M200	—	9.0	60.0	10.0	1.0	2.0	5.0	—	12.0	0.15	—
738	—	16.0	61	8.5	0.9	3.4	3.4	1.7	2.6	0.17	—
X-750	7.0	15.5	73.0	—	1.0	2.5	0.7	—	—	0.04	0.2
718	18.5	19.0	52.5	—	5.1	0.9	0.5	3.0	—	0.04	0.2

APPENDIX

Table 2A. Stress Rupture Test Data I.

Sample	Temp. (°C)	Stress (MPa)	Rupture Time (hours)	O ₂ (ppm)	μ O ₂ (kcal/mole)	H ₂ O (v) (ppm)	HVN (300 g)	Percent Intergranular Fracture
30P	550	644	478.3	STOP	1.2	NA	394.7	Stop Not Fractured
4P	650	650	96.4	< 0.01	-33.78	< 2.0*	487.7	0%
3P	650	708	71.7	STOP	0.04	< 2.0*	449.6	Stop Not Fractured
37P	650	542	452.5	0.5	-26.61	NA	466	4%
38P	650	542	522	STOP	0.5	NA	471.5	Stop Not Fractured
33P	650	640	174.3	0.75	-25.86	NA	486.8	<=1
8P	650	538	211	STOP	0.9	< 2.0*	485.7	Stop Not Fractured
34P	650	640	142.4	0.92	-25.49		454.5	4%
31P	650	640	71.7	1	-25.34	NA	503.9	8%
32P	650	0		1		NA	484.1	0 % No Load Fracture At R.T.
20cw-26	650	650	428.2	STOP	3	0.3	530.8	0% Broken After Test At R.T.
39P	650	644	119.1	STOP	4.45	0.8	478.6	Stop Not Fractured
9P	650	640	82.35	5.97	-22.06	< 2.0*	486.2	23%
66T	650	642	61.5	STOP	6	< 2.0*	476.4	Stop Not Fractured
60P	650	650	188	STOP	35.5	2.6	520.8	19.4% Broken After Test At R.T.
61P	650	648	118	STOP	37	1.5	484.1	0% Broken After Test At R.T.
62P	650	650	122		38	3.5	492	40.40%
45P	650	650	135.9		39	3.5	512.95	45%
20cw-25	650	650	114.2	STOP	44	1	537	0% Broken After Test At R.T.
5P	650	652	44.1		53	< 2.0*	473.3	41%
63P	650	650	114.2		195	3.5	514.8	47.80%
1A	650	469	12.3	1000	-12.67	1.6	498.5	73.6
49P	650	650	28.3	1000	-12.67	1.6	499.5	61%

* Analyzed Gas, NA = Water vapor detector not available at time of test.

APPENDIX

Table 2A. Stress Rupture Test Data I continued.

Sample	Temp. (°C)	Stress (MPa)	Rupture Time (hours)	O ₂ (ppm)	μ O ₂ (kcal/mole)	H ₂ O (v) (ppm)	HVN (300 g)	Percent Intergranular Fracture
22P	650	650	44.7	STOP	1000	-12.67	452.6	0% Broken after test at R.T.
20CW-24	650	650	3.65	1000	-12.67	6	513.1	57%
1B	650	650	4.05	1000	-12.67	6	512.9	65%
20CW-31	650	469	7.3	1000	-12.67	1.7	534.1	72%
20CW-30	650	469	7.85	1000	-12.67	1.7	534.1	72.50%
23P	650	469	77	1000	-12.67	1.9	509	Stop Not Fractured
24P	650	650	111.4	1000	-12.67	0.7	513.7	58.50%
10CW-2	650	469	8.2	1000	-12.67	0.9	515.1	73.40%
SA-1	650	469	102.8	1000	-12.67	1.2	508.3	1.9% Broken After Test At R.T.
			STOP					
7P	700	589	22.2	0.42	-28.39	< 2.0*	480.9	0%
36P	700	0		0.95			441.7	No Load Fracture At R.T.
35P	700	538	27	0.95	-26.81		440.3	0%
6P	700	639	3.45	53	-19.03	< 2.0*	493.1	27%
46P	700	650	3.1	195	-16.51	3.5	480	40%
64P	700	650	1.6	195	-16.51	3.5	471.6	40%
65P	750	650	0.07	195 ppm	-17.36	3.5	444.8	1.70%
20P	750	551	0.45	195 ppm	-17.36	3.5	456.6	24%
21P	750	450	2.4	195 ppm	-17.36	3.5	447.9	34%

* Analyzed Gas, NA = Water vapor detector not available at time of test.

APPENDIX

Table 3A. Stress Rupture Data II.

Sample	R. A. (%)	Ductile Area (mm ²)	Intergranular Area (mm ²)	Oxidation Depth (mm)	Grain Diameter(s) (μ m)	Annotations
30P					14.5	
4P	6.6%	13.10			14.5	
3P					14.5	
37P	14.5%	10.88	0.44	0.08	14.5	
38P				0.05	14.5	
33P	13.0%	13.00			14.5	
8P					14.5	
34P	21.3%	10.52	0.50	0.08	14.5	
31P	14.0%	10.40	0.87	0.15	14.5	
32P	0.0%	14.70			14.5	Sample not loaded during test w/ 31P
20cw-26					Duplex	Double notch round bar 20% Cold Work, Sample Broke Open After Test
39P					14.5	
9P	9.5%	9.72	2.96	0.45	14.5	
66T					14.5	
60P	24.8%	8.06	1.94	0.40	14.5	Broken open after test
61P	12.6%	12.23			14.8	
62P	23.3%	6.31	4.27	0.77	14.5	
45P	17.6%	5.70	4.57	0.78	14.5	Sample H.T. in 1×10^{-6} Torr vacuum at 650 C for 200h then tested
20cw-25	11.0%				Duplex	Double notch round bar 20% Cold Work, Sample Broke Open After Test
5P	21.0%	6.15	4.00	0.72	14.5	
63P	5.1%	7.00	6.40	1.04	14.5	

APPENDIX

Table 3A. Stress Rupture Data II continued.

Sample	R.A. (%)	Ductile Area (mm ²)	Intergranular Area (mm ²)	Oxidation Depth (mm)	Grain Diameter(s) (μ m)	Annotations
1A	2.3%	11.22	31.34	1.79	Duplex	Double notched round bar H.T. in 1×10^{-6} Torr vacuum at 650 C for 200h
49P	9.8%	4.71	7.44	1.26	14.2	H.T. at 650 C for 200h in 1×10^{-6} torr vacuum then tested
22P	22.0%	10.74			14.5	Test stopped sample broke in air at room temperature
20cw-24	2.3%	15.00	20.00	1.15	Duplex	Double notch round bar no heat treatment prior to test 20% Cold Work
1B	6.0%	13.48	24.59	1.41	Duplex 25.2 small, 220 large	Sample H.T. at 650 C for 200h in 1×10^{-6} torr vacuum then tested
20cw-31	14.0%	11.44	29.69	1.71	Duplex 15.8 small, 534 large	Double notch round bar no heat treatment prior to test 20% Cold Work
20cw-30	17.0%	11.55	30.50	1.74	Duplex	Double notch round bar no heat treatment prior to test 20% Cold Work
23P					14.5	
24P	0.3%	5.79	8.22	1.25	14.5	
10CW-2	18.0%	11.13	31.22	1.79	Duplex	Double notch round bar 10% Cold Work
SA-i	11.0%	27.63	0.55	0.03	22.5	Double notch round bar Solution Annealed, Sample Broke Open After Test

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