CORROSION FATIGUE BEHAVIOR OF
AUSTENITIC-FERRITIC STAINLESS STEELS

by

JEROME ALAN MOSKOVITZ

B.S., Georgia Institute of Technology
1973

S.M., Massachusetts Institute of Technology
1975

Submitted in partial fulfillment of the requirements

for the degree of

DOCTOR OF PHILOSOPHY

at the

Massachusetts Institute of Technology

September, 1977

Signature Redacted

Signature of Author.

Department of Materials Science and Engineering

August 12, 1977

Signature Redacted

Certified by.

Signature Redacted

Thesis Supervisor

Accepted by.

Chairman, Departmental Committee on Graduate Students

ARCHIVES

ABSTRACT

CORROSION FATIGUE BEHAVIOR OF
AUSTENITIC-FERRITIC STAINLESS STEELS

by

JEROME ALAN MOSKOVITZ

Submitted to the Department of Materials Science and Engineering on
August 12, 1977, in partial fulfillment of the requirements for the
Degree of Doctor of Philosophy

The corrosion fatigue behavior of austenitic-ferritic stainless steels was studied in air and in acidic chloride solution. Both commercially available cast alloys and an experimental tie-line series of five wrought alloys were investigated. Smooth bar reversed bending tests showed the wrought alloy containing 64% ferrite to have the best overall corrosion fatigue resistance. Fatigue crack growth rate studies showed the 64% alloy also has the best resistance to crack growth in solution at a stress ratio of $R = 0.05$, but that a fully ferritic alloy is more resistant at $R = 0.6$. The acceleration of crack growth by the corrosive environment at $R = 0.05$ is due to the electrochemical dissolution of austenite at the crack tip in ferritic-matrix alloys, and at $R = 0.6$ to stress corrosion cracking in the austenite for alloys containing over 30% austenite. There were no dissolution effects on crack growth in the cast alloys due to their coarse microstructure, however, stress corrosion cracking effects did occur.

The mechanism of corrosion fatigue crack initiation was investigated by room temperature creep tests on 310 stainless steel wire, performed during anodic dissolution. These tests showed that near-surface plastic deformation is accelerated by surface dissolution without any rupture of the surface passive layer. These findings support the general theory that corrosion fatigue crack initiation is due to the dissolution-accelerated formation of persistent slip bands, which develop into fatigue crack nuclei. Crack initiation in the austenitic-ferritic alloys was shown to occur by this mechanism.

Thesis Supervisor: Regis M. Pelloux

Title: Professor of Metallurgy

TABLE OF CONTENTS

<u>Chapter Number</u>		<u>Page Number</u>
	Title Page	1
	Abstract	2
	Table of Contents	3
	List of Figures	6
	List of Tables	11
	Acknowledgements	12
I.	INTRODUCTION	13
II.	LITERATURE SURVEY	17
	A. The Phenomena of Corrosion Fatigue	17
	1. Corrosion Fatigue Crack Initiation	17
	2. Near-Threshold Behavior	25
	3. Corrosion Fatigue Crack Propagation	27
	B. Metallurgy of Austenitic-Ferritic Stainless Steels	30
	1. Physical Metallurgy	30
	2. Corrosion and Stress Corrosion Cracking Behavior	35
	3. Fatigue and Corrosion Fatigue Behavior	37
III.	MATERIALS AND TEST PROCEDURES	41
	A. Description of Alloys	41
	B. Tensile Tests	49
	C. Fatigue Crack Growth Rate Tests	49
	D. Smooth Bar S-N Tests	51
	E. Notched Bar S-N Tests	54

<u>Chapter Number</u>	<u>Page Number</u>
F. Abrading Electrode Tests	56
G. Creep Tests Under Anodic Dissolution	59
H. Anodic Polarization Curves	62
I. Fractography	62
IV. RESULTS	64
A. Tensile Tests	64
B. Fatigue Crack Growth Rate Tests	64
1. Commercial Alloys	64
2. Tie-Line Series Alloys	67
C. Smooth Bar S-N Tests	81
D. Notched Bar S-N Tests	85
E. Abrading Electrode Tests	87
F. Creep Tests Under Anodic Dissolution	91
G. Fractography	95
1. Smooth Bar Crack Initiation Surfaces - IN-744 Tie-Line Series Alloys	95
2. Fracture Surfaces - IN-744 Tie-Line Series Alloys	99
3. Fracture Surfaces - Commercial Alloys	114
V. DISCUSSION	121
A. Environmental Acceleration of Fatigue Crack Initiation	121

<u>Chapter Number</u>		<u>Page Number</u>
	B. The Effect of Microstructure on the Corrosion Fatigue Behavior of Austenitic-Ferritic Stainless Steels	126
	1. The Effect of Microstructure on Crack Initiation	129
	2. The Effect of Microstructure on Crack Propagation	134
	3. The Best Microstructure for Corrosion Fatigue Resistance	139
VI.	CONCLUSIONS	142
VII.	SUGGESTIONS FOR FURTHER WORK	144
VIII.	REFERENCES	145
	Appendix: Procedure for Normalization of Creep Data	151
	Biographical Note	152

LIST OF FIGURES

<u>Figure Number</u>		<u>Page Number</u>
1	Slip-dissolution-reverse slip model of corrosion fatigue crack initiation. From Pyle, Rollins, and Howard (33).	22
2	Enhanced slip model of corrosion fatigue crack initiation.	24
3	1100° isotherm of the Fe-Ni-Cr ternary phase diagram. From ASM Metals Handbook (69).	31
4	Schaeffler diagram for stainless steel weld metal (70).	32
5	Variation in volume fraction ferrite as a function of alloying elements. From Jolly (73).	34
6	Variation in volume fraction ferrite as a function of quenching temperature. From Jolly (73).	34
7	Dependence of fatigue limit on volume fraction ferrite, IN-744 tie-line series. From Hayden and Floreen (87).	39
8	Microstructure of cast alloy VK-A171.	44
9	Microstructure of cast alloy VK-A271.	44
10	Microstructure of wrought alloy Uranus 50.	45
11	Microstructure of Heat 224 (100% ferrite).	46
12	Microstructure of Heat 225 (79% ferrite).	46
13	Microstructure of Heat 226 (64% ferrite).	47
14	Microstructure of Heat 227 (34% ferrite).	47
15	Microstructure of Heat 229 (6% ferrite). a) unetched b) etched to reveal austenite grain size.	48
16	Double cantilever beam fatigue crack propagation specimen.	50
17	Single-edge-notch fatigue crack propagation specimen.	52
18	Bending fatigue specimen.	53
19	Notched bar S-N fatigue specimen.	55

<u>Figure Number</u>		<u>Page Number</u>
20	Design of electrode used in abrading electrode experiments.	57
21	Apparatus used in abrading electrode experiments.	58
22	Creep testing apparatus.	60
23	Dependence of tensile properties on volume fraction ferrite, IN-744 tie-line series alloys.	65
24	Fatigue crack growth rate curves, VK-A271, showing effect of stress ratio.	66
25	Fatigue crack growth rate curves, Uranus 50, showing effect of specimen orientation.	68
26	Fatigue crack growth rate curves, Heat 224.	69
27	Fatigue crack growth rate curves, Heat 225.	70
28	Fatigue crack growth rate curves, Heat 226.	71
29	Fatigue crack growth rate curves, Heat 227.	72
30	Fatigue crack growth rate curves, Heat 229.	73
31	Fatigue crack growth rate curves, tie-line series alloys, air, $R = 0.05$.	74
32	Fatigue crack growth rate curves, tie-line series alloys, white water, $R = 0.05$.	75
33	Fatigue crack growth rate curves, tie-line series alloys, air, $R = 0.6$.	76
34	Fatigue crack growth rate curves, tie-line series alloys, white water, $R = 0.6$.	77
35	Dependence of ΔK_{th} on volume fraction ferrite for the tie-line series alloys.	78
36	Dependence of ΔK required to cause a crack growth rate of 5×10^{-6} in/cycle (1.25×10^{-7} m/cycle) on volume fraction ferrite for the tie-line series alloys.	79

<u>Figure Number</u>		<u>Page Number</u>
37	Dependence of ΔK required to cause a crack growth rate of 5×10^{-5} in /cycle (1.25×10^{-6} m/cycle) on volume fraction ferrite for the tie-line series alloys.	80
38	Dependence of fatigue lifetime on volume fraction ferrite, tie-line series alloys, 52,000 PSI (358.5 MPa).	82
39	Dependence of fatigue lifetime on volume fraction ferrite, tie-line series alloys, 55,000 PSI (379.2 MPa).	83
40	Dependence of fatigue lifetime on volume fraction ferrite, tie-line series alloys, 60,000 PSI (413.7 MPa).	84
41	Notched bar S-N data, VK-A271.	86
42	Abrading electrode test data. Change in electrochemical potentials with time after both electrodes were abraded.	88
43	Abrading electrode test data. Change in electrochemical potential with time after only the ferrite electrode was abraded.	89
44	Abrading electrode test data. Change in electrochemical potential with time after only the austenite electrode was abraded.	90
45	Anodic polarization diagrams in 3.5% NaCl, Heats 224 (100% ferrite) and 229 (94% austenite).	92
46	Typical curve of creep elongation as a function of time for various applied anodic current densities. 310 stainless steel wire in a 30% $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ solution at 12°C . Applied stress is 46,750 PSI (322.4 MPa).	93
47	Dependence of creep rate on anodic current density for 310 stainless steel in 30% $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ solution.	94
48	SEM micrographs of surface of 310 stainless steel wire following creep test under anodic dissolution in FeCl_2 solution.	96
49	Dependence of creep rate on anodic current density for 310 stainless steel in 5N H_2SO_4 + .5N NaCl solution.	97

<u>Figure Number</u>		<u>Page Number</u>
50	Anodic polarization diagrams in the range of active potentials for 310 stainless steel wire in 5N H ₂ SO ₄ + .5N NaCl solution.	98
51	Crack initiation at PSB and grain boundaries, Heat 224.	100
52	Crack initiation at PSB in ferrite, Heat 225.	101
53	Crack initiation at PSB in both phases, Heat 226.	101
54	Crack initiation at PSB in austenite, Heat 227.	102
55	Crack initiation at PSB in austenite, Heat 229.	102
56	Fracture surface, Heat 224, air, R = 0.05, $\Delta K = 25 \text{ KSI}\sqrt{\text{in}}$ (27.5 MPa $\sqrt{\text{m}}$).	103
57	Fracture surface, Heat 224, air, R = 0.05, $\Delta K = 37 \text{ KSI}\sqrt{\text{in}}$ (40.7 MPa $\sqrt{\text{m}}$).	104
58	Fracture surface, Heat 224, air, R = 0.6, $\Delta K = 16 \text{ KSI}\sqrt{\text{in}}$ (17.6 MPa $\sqrt{\text{m}}$).	104
59	Fracture surface, Heat 225, air, R = 0.05, $\Delta K = 23 \text{ KSI}\sqrt{\text{in}}$ (25.3 MPa $\sqrt{\text{m}}$).	105
60	Fracture surface, Heat 225, white water, R = 0.05, $\Delta K = 19 \text{ KSI}\sqrt{\text{in}}$ (20.9 MPa $\sqrt{\text{m}}$).	106
61	Fracture surface, Heat 225, air, R = 0.05, $\Delta K = 59 \text{ KSI}\sqrt{\text{in}}$ (64.9 MPa $\sqrt{\text{m}}$).	107
62	Fracture surface, Heat 225, air, R = 0.6, $\Delta K = 18.5 \text{ KSI}\sqrt{\text{in}}$ (20.4 MPa $\sqrt{\text{m}}$).	107
63	Fracture surface, Heat 226, white water, R = 0.05, $\Delta K = 22 \text{ KSI}\sqrt{\text{in}}$ (24.2 MPa $\sqrt{\text{m}}$).	109
64	Fracture surface, Heat 226, R = 0.6 a) air, $\Delta K = 17.5 \text{ KSI}\sqrt{\text{in}}$ (19.3 MPa $\sqrt{\text{m}}$) b) white water, $\Delta K = 16 \text{ KSI}\sqrt{\text{in}}$ (17.6 MPa $\sqrt{\text{m}}$).	110
65	Fracture surface, Heat 227, air, R = 0.05, $\Delta K = 19 \text{ KSI}\sqrt{\text{in}}$ (20.9 MPa $\sqrt{\text{m}}$)	111
66	Fracture surface, Heat 227, white water, R = 0.6, $\Delta K = 14 \text{ KSI}\sqrt{\text{in}}$ (15.4 MPa $\sqrt{\text{m}}$)	111

<u>Figure Number</u>		<u>Page Number</u>
67	Fracture surface, Heat 229, air, $R = 0.05$, $\Delta K = 19 \text{ KSI}\sqrt{\text{in}}$ ($20.9 \text{ MPa}\sqrt{\text{m}}$).	112
68	Fracture surface, Heat 229, air, $R = 0.6$, $\Delta K = 30 \text{ KSI}\sqrt{\text{in}}$ ($33.0 \text{ MPa}\sqrt{\text{m}}$).	112
69	Fracture surface, Heat 229, white water, $R = 0.05$, $\Delta K = 21 \text{ KSI}\sqrt{\text{in}}$ ($23.1 \text{ MPa}\sqrt{\text{m}}$).	113
70	Fracture surface, Heat 229, white water, $R = 0.6$, $\Delta K = 14.8 \text{ KSI}\sqrt{\text{in}}$ ($16.3 \text{ MPa}\sqrt{\text{m}}$).	113
71	Fracture surface, VK-A271, $R = 0.05$, low ΔK .	116
72	Fracture surface, VK-A271, $R = 0.05$, high ΔK .	117
73	Fracture surface, VK-A271, $R = 0.6$, white water, oriented for cleavage in ferrite.	118
74	Fracture surface, Uranus 50, RW orientation, $\Delta K = 24 \text{ KSI}\sqrt{\text{in}}$ ($26.4 \text{ MPa}\sqrt{\text{m}}$).	119
75	Fracture surface, Uranus 50, WR orientation, $\Delta K = 19 \text{ KSI}\sqrt{\text{in}}$ ($20.9 \text{ MPa}\sqrt{\text{m}}$).	119

LIST OF TABLES

<u>Table No.</u>		<u>Page No.</u>
1	Composition of Alloys: a) Commercial Alloys b) IN-744 Tie-Line Series Alloys	42
2	Mechanical Properties of Commercial Alloys	43
3	Summary of Fracture Surfaces at Low ΔK for Tie-Line Series Alloys	115

ACKNOWLEDGEMENTS

The author is grateful to a number of people and organizations for assistance and encouragement throughout the course of his graduate education.

To Professor R. M. Pelloux, his thesis advisor, for his continuing support, tolerance, and guidance,

To Professor R. M. Latanision and Professor H. H. Uhlig, for their invaluable technical guidance concerning the theoretical portions of this research,

To Professors R. M. Rose and R. M. Latanision, members of the thesis committee, for their review of the manuscript,

To I. Puffer and L. Sudenfield, for their technical assistance in the experimental phases of this research,

To Valmet Oy of Finland for providing partial financial support for this research,

To INCO, Ltd., for fellowship support during the latter part of this research,

To Professor W. Owen and the Department of Materials Science and Engineering for additional financial support,

To P. Shearer, A. King, and J. Boughton for assistance in preparation of the rough manuscript,

To J. Boughton for typing the final manuscript,

To J. Mara for preparing the drawings,

And to most of the members of the Fatigue Group for their assistance and support.

I. INTRODUCTION

The development of austenitic-ferritic (also referred to as duplex or $\alpha - \gamma$) stainless steels has been motivated by the need for alloys that can withstand high stresses (both static and cyclic) in corrosive environments, i.e. materials having good stress corrosion cracking (SCC) and corrosion fatigue resistance. These high strength, corrosion-resistant stainless steels are or will be used extensively in the chemical, nuclear and papermaking industries. Austenitic stainless steels, such as types 304 and 316, have a rather limited fatigue strength because of their low yield strength. They are also quite susceptible to SCC in a variety of mildly corrosive environments, and to intergranular corrosion if not properly heat treated. Ferritic stainless steels, such as types 430 and 446, have low ductility and toughness, which leads to high fatigue crack propagation rates. The martensitic alloys, such as type 410, have relatively higher yield strengths, good fracture toughness in the tempered condition, but low chromium content which significantly limits their corrosion resistance.

Austenitic-ferritic stainless steels were first produced as cast alloys, and their corrosion and SCC resistance were first studied in detail in the early 1960's (1). The evaluation of some recently developed casting alloys (2-4) has shown them to perform very well in applications requiring resistance to corrosion fatigue in acidic chloride solutions. However, the production of large castings, such as suction-press rolls for the papermaking industry, requires a rapid quenching step to maintain the high temperature duplex microstructure. This rapid quench creates

high residual tensile stresses which will be superimposed on the normal operating cyclic stresses, and can lead to accelerated fatigue failure. Furthermore, microstructural control in these casting alloys is quite difficult. Opportunities to improve SCC, fatigue, and corrosion resistance through variations in the cast microstructure are thus rather limited. Consequently, the wrought $\alpha - \gamma$ alloys were developed as an alternative to the cast alloys as they offer the prospect of increased microstructural control. However, these wrought alloys must be welded to produce useful components, and great care must be taken in processing to control the microstructures of the weld metal and of the heat affected zone.

This research program was undertaken to correlate the microstructural parameters of $\alpha - \gamma$ stainless steels to their corrosion fatigue behavior. The following corrosion fatigue characteristics were determined:

1. overall corrosion fatigue resistance as exhibited in stress amplitude vs. cycles-to-failure (S-N) testing
2. corrosion fatigue crack initiation behavior, for smooth and notched bars
3. corrosion fatigue crack propagation rates
4. values of the threshold alternating stress intensity factor for non-propagating cracks, ΔK_{th} .

Particular emphasis has been placed on the dependence of corrosion fatigue behavior on metallurgical variables, primarily volume fraction of ferrite and microstructural orientation of the two phases. The effect of electrochemical dissolution on crack initiation was evaluated, and will

be discussed in light of existing theories of corrosion fatigue crack initiation. One key point considered is whether rupture of a passive film is necessary for corrosion-accelerated crack initiation to occur in stainless steels. This point was investigated by observing crack initiation mechanisms in corrosion fatigue tests, and through a study of room temperature creep deformation during electrochemical dissolution. Crack initiation from shallow notches was also investigated, along with crack propagation behavior near ΔK_{th} . Since corrosion fatigue behavior in this near-threshold region is quite sensitive to a mean tensile stress, the effect of mean stress on ΔK_{th} and on fatigue crack propagation rates was studied through variations in the stress ratio R , where $R = \sigma_{min}/\sigma_{max}$.

An assessment of the synergistic interactions between mechanical fatigue and corrosion at a smooth surface or at a crack tip requires a detailed understanding of the nature of the galvanic couple between the austenite and ferrite phases, and of its role in the crack initiation and crack propagation stages. The nature of this couple must be understood as a function of the volume fraction of each phase. The galvanic couple between pure austenite and pure ferrite in both the oxide-free active state and in the oxide-covered passive state was studied by an abrading electrode technique in order to determine the electrochemical driving force existing at the smooth metal surface and at the tip of an advancing corrosion fatigue crack.

The goal of this thesis is to correlate the mechanical, metallurgical, and electrochemical factors which control the corrosion fatigue behavior of austenitic-ferritic stainless steels. This correlation should provide some sound guidelines to define the duplex microstructures having

the best corrosion fatigue resistance. The experimental data will also serve to improve our understanding of the basic mechanisms of corrosion fatigue in stainless steels.

II. LITERATURE SURVEY

This literature survey is divided into two sections. The first section reviews various aspects of corrosion fatigue theories as they relate to crack initiation, to the threshold stress intensity factor for non-propagating cracks, and to crack propagation rates. The second section reviews the physical metallurgy of austenitic-ferritic stainless steels and their corrosion, stress corrosion cracking, and fatigue and corrosion fatigue behavior.

A. The Phenomena of Corrosion Fatigue

Corrosion fatigue is best described as a synergistic interaction of cyclic stress and corrosive environment resulting in a mechanical damage which occurs more rapidly than the sum of the two individual effects. A recent symposium volume (5) deals with the various aspects of corrosion fatigue in detail. Pelloux et al (6) have recently reviewed corrosion fatigue phenomena by discussing some of the unknowns remaining to be studied. Environmental effects are apparent in all the various stages of fatigue failure: crack initiation, near-threshold crack growth behavior, and crack propagation. Each of these regions will be discussed individually in the following survey.

1. Corrosion Fatigue Crack Initiation

The process of corrosion fatigue, which has been reviewed extensively by Laird and Duquette (7), can be most simply described as the perturbation of the normal fatigue crack initiation mechanisms by environmental interactions. In order to discuss the mechanism of corrosion fatigue crack initiation, the process by which fatigue crack initiation

occurs in the absence of a corrosive environment must first be dealt with. Fatigue crack initiation generally occurs through the development of near-surface dislocation arrangements and formation of persistent slip bands (PSB), which act as crack nuclei (7).

The dislocation arrangements leading to the formation of PSB have been studied extensively, mostly in the case of pure metal single crystals. Wei and Baker (8,9) showed for polycrystalline iron that initial fatigue damage, which is confined to regions near the specimen surface, takes the form of planar arrays of dislocation loops and intense deformation bands of tangled dislocations. These features correspond with the coarse slip markings observed on the metal surface. Lukas and Klesnil (10) have observed a ladder-like dislocation structure within PSB in FCC metals. In a recent review, Grosskreutz and Mughrabi (11) note that one must differentiate between the dislocation structures in the bulk and within the PSB. In the bulk, the dislocations are arranged in veins or bands of dipoles, or in cell walls, depending on the cyclic strain amplitude. This arrangement has been observed not only in the bulk away from PSB, but also within 500-1000 Å of the free surface. Within the PSB, a well-defined ladder or cell structure exists. The development of the bulk dislocation structure into PSB has been studied extensively (10,12). When the matrix dislocation structure previously described approaches instability, dislocations released from the deteriorating matrix structure and newly generated dislocations will merge to form dipolar walls, providing the framework for the ladder structure. Because the matrix structure is so close to instability, this process can occur rapidly over a few cycles (13). The

ladder structure evolves as dislocations transfer from one dipolar wall surface across the between-wall channel to the opposing wall surface to accommodate the fatigue strain. When the stable ladder structure is formed, screw dislocation packets can move in the channels towards the free surface. When they reach the surface they will be annihilated and reform on the return half-cycle. If the reformed packet returns along a different channel, a net displacement results at the free surface. After several such instances of alternating slip displacement, intrusions and extrusions become observable. This transfer of slip from one set of planes to another can also be triggered by any inhomogeneity at the surface (12). This demonstrated formation of PSB in surface layers initially free from dislocations is contradicted by the work of Kramer and Kumar (14), who claim the existence of a surface debris layer. Laird (15-16) has shown that in copper there is a minimum fatigue strain necessary to produce a single PSB. This strain value corresponds to the beginning of a plateau in the cyclic stress-strain curve and therefore it defines a fatigue stress limit. The lack of PSB formation will indefinitely delay crack initiation in "clean" materials.

As it has been shown that PSB formation is extremely sensitive to surface conditions (12), it follows that any type of surface phenomena, either mechanical or chemical, may affect fatigue crack initiation. This effect can be due to the presence of a mechanically deposited surface film, a chemically stable surface oxide, or surface dissolution due to corrosion reactions. The latter two phenomena are particularly important in corrosion fatigue crack initiation, as will be discussed in detail in the following paragraphs. The role of these surface effects in the

mechanical behavior of solids is dealt with extensively in a recent symposium volume (17), and was previously studied by Russian investigators (18).

Grosskreutz (19) has summarized the effect of surface films on fatigue crack initiation. Studies by Greenfield et al (20-23) have shown that the surface deposition of a thin layer (500 Å) of metal followed by surface alloying can change greatly the near-surface plastic deformation characteristics of pure copper by inducing the formation of a network of accommodation dislocations which act as barriers to slip activity. The resulting dislocation tangles beneath the surface layer retard the localization of slip required to form fully developed PSB, causing a decrease in PSB spacing and delaying crack initiation considerably. Other studies have supported these observations (24,25).

The effect of anodic oxide layers on the mechanical behavior of aluminum was studied in detail by Leach et al (26,27) who showed a strengthening effect. Grosskreutz has shown that oxide films affect the dislocation-surface interactions in aluminum (28), and that the fracture behavior of oxide films on aluminum is sensitive to the environment (29). Sethi and Gibala (30) have shown similar strengthening effects for oxide-coated niobium crystals. It appears that the effect of these anodic oxide layers is very similar to that of the mechanically deposited surface layers studied by Greenfield et al.

Environmental interactions are, by nature, surface interactions, so that any corrosive reaction will strongly influence the previously discussed near-surface dislocation phenomena. An active environment can either affect the formation of PSB, or affect the mechanisms by which a

crack develops from these PSB. Howard and Pyle (31) have demonstrated a relationship between PSB spacing and electrochemical dissolution rate at a metal surface, with PSB spacing decreasing with decreasing dissolution rate. This effect could possibly be due to a variation in the thickness of a passive surface oxide layer with dissolution rate, the passive oxide acting to delay localization of slip into PSB, similar to the coatings of Greenfield et. al. (20-23). Alternatively, it can be said that PSB form independently of any environmental effects, and that the role of the environment is to accelerate the process by which PSB lead to fatigue crack initiation. This acceleration can occur by any of three processes:

(1) preferential dissolution at the PSB because the PSB are anodic to the matrix material; (2) rupture of the passive film by emerging PSB causing the exposure of fresh metal; (3) localized dissolution resulting in marked local changes in dislocation arrangement, affecting the intrusion-extrusion development within the PSB. Pyle, Rollins and Howard (32,33) have proposed, on the basis of studies of dissolution transients associated with cyclic plastic straining, an initiation mechanism of slip-dissolution-reverse slip at PSB to explain the relationship between PSB spacing and dissolution rate. This model, shown in Figure 1, has as its central feature the dissolution of metal at freshly exposed slip steps resulting in the formation of corrosion induced notches which act as crack nuclei. Moskovitz (34), however, has shown that at a constant alternating stress, PSB in austenitic-ferritic stainless steels develop more rapidly in the presence of a corrosive environment. This observation is consistent with the process of dissolution of the surface oxide layer resulting in enhanced PSB formation. A model for this process was first proposed by

Figure 1: Slip-dissolution-reverse slip model of corrosion fatigue crack initiation. From Pyle, Rollins, and Howard (33).
 a) dissolution occurs on face of exposed slip step
 b) load reversal drives step back into surface, producing wedge shaped crack on slip plane
 c) and d) if reverse slip occurs on different planes, many atomic layers must be removed for a crack to develop.

Duquette and Uhlig (35), in which the surface dissolution simply reduces the barrier to slip activity, as shown in Figure 2. This model accounts for the existence of a critical anodic current density, below which there are no effects of dissolution on fatigue life. Critical anodic current densities have been measured in numerous studies (35-38). In one such study, the increase in slip activity due to dissolution was attributed to the production of divacancies which induce climb in sessile dislocations (37). The preferential dissolution of active slip bands can also lead to slip intensification (39). Duquette et. al. (39-41) have studied the effect of surface dissolution on the near-surface dislocation structure. The near-surface dislocation structure in OFHC copper was found to have a more developed cell arrangement in air than in NaCl solution, the difference being large enough to affect PSB formation.

Other investigators have shown definite environmental effects during static deformation preceding any crack initiation. Latanision and Westwood have reviewed these studies in detail (42). Latanision, Oppenhauser, and Westwood (43) have shown that the microhardness of zinc single crystals in an electrolyte is dependent on electrochemical potential. Latanision and Staehle (44) have developed a model for enhanced plastic deformation based on the activation of near-surface dislocation sources, supported by an observed increase in slip line spacing on nickel single crystals tensile tested under active dissolution as compared to those tested in air. Uhlig et. al. (37,45) have demonstrated an acceleration of the room temperature creep rate of copper and iron wires with increasing anodic dissolution. There is reasonable

Figure 2: The enhanced slip model of corrosion fatigue crack initiation. Surface dissolution in the vicinity of slip steps removes dislocation locking sites, thereby enhancing slip activity which leads to fatigue crack initiation.

support for the extension of this phenomenon into the regime of cyclic deformation.

Additional phenomena can further complicate the process of corrosion fatigue crack initiation. Prowse and Wayman (46) propose that hydrogen embrittlement effects are responsible for accelerated corrosion fatigue failure in a medium carbon steel. Staehle (47) notes that in many cases corrosion fatigue and SCC cannot be separated. The superposition of a mean stress on cyclic stresses produces additional complications, as SCC effects become much more significant in the presence of a mean tensile stress. Consideration must also be given to the near-surface state of stress (ratio of tensile to shear stress) on corrosion fatigue crack initiation mechanisms. This can be done by notched bar tests, such as those performed by Barsom and McNicol (48). Similar studies have yet to be done for corrosion fatigue.

2. Near-Threshold Behavior

The early stage of crack growth following crack initiation is studied either by S-N testing of notched fatigue specimens or by carrying out conventional fatigue crack growth rate (FCGR) studies. The transition from crack initiation to crack propagation is extremely important to our understanding of corrosion fatigue because a great percentage of lifetime may be spent in this region ($<10^{-8}$ m/cycle). For a given alloy in a given environment, one can generally find a value of ΔK below which crack propagation will not occur, denoted ΔK_{th} . Barsom and McNicol (48) have studied in detail the effect of notch geometry on ΔK_{th} for a martensitic steel. They conclude that in a bar containing a notch of root radius ρ , there is a critical value of the parameter $\Delta K/\sqrt{\rho}$ below which

there will not be fatigue failure. However, small non-propagating cracks may be initiated at $\Delta K/\sqrt{\rho}$ values less than the critical value.

It is in this transition region that the influence of mean stress becomes increasingly important. Klesnil and Lukas (49) have proposed an empirical relationship between ΔK_{th} and R, the cyclic stress ratio of $\sigma_{min}/\sigma_{max}$, of the form:

$$\Delta K_{th} = \Delta K_{th_0} (1 - R)^\gamma$$

where ΔK_{th_0} is defined for $R = 0$ and γ is an empirical material constant. For ferritic-pearlitic steels, Masounave and Bailon (50) found the relationship to be valid for a value of $\gamma = 1$, reducing the equation to a simpler form:

$$\Delta K_{th} = \Delta K_{th_0} (1 - R)$$

There have been no corrosion fatigue studies which have dealt specifically with this threshold region. Ritchie (51), however, has studied near-threshold propagation in an ultra-high strength steel in humid air. He found that increases in R and increases in material strength independently lead to a decrease in ΔK_{th} and an increase in near-threshold growth rates. This behavior is explained on the basis of hydrogen embrittlement due to the presence of moist air at the crack tip. Dawson and Pelloux (52) have shown a dependence of crack growth at ΔK values just above the threshold region on SCC resistance in $\alpha - \beta$ titanium alloys. A definitive study of corrosion fatigue effects on ΔK_{th} is necessary to bridge the gap between known crack initiation and crack propagation effects.

3. Corrosion Fatigue Crack Propagation

There are generally considered to be two types of corrosion-accelerated mechanisms of fatigue crack propagation. The simplest mechanism assumes a direct superposition of stress corrosion crack growth and fatigue crack growth ignoring any synergistic effects. This mechanism can occur only above the threshold stress intensity for SCC, K_{ISCC} . Given any cyclic loading with the maximum stress intensity above K_{ISCC} , one can calculate the amount of time per cycle spent above K_{ISCC} , calculate the increment of stress corrosion crack growth per cycle, and add it to the mechanical fatigue component to obtain the total growth rate (53,54). It has been suggested that this approach is valid only when the SCC and mechanical components are approximately equal (55).

Although there is little doubt that SCC effects play a role in accelerating FCGR in a corrosive environment, environmentally accelerated FCGR is also observed below K_{ISCC} and in materials that are immune to SCC. For example Misawa, Ringshall, and Knott (56) found different activation energies for the corrosion component of crack growth below and above K_{ISCC} for a low carbon steel in deaerated distilled water. This "true corrosion fatigue" phenomena, which involves dynamic interaction of strain and environment at a growing fatigue crack tip, may be similar to environmental effects discussed for crack initiation, and it can occur both below and above K_{ISCC} . Endo and Komai (57), studying crack growth using different cyclic wave forms, have shown that the major portion of crack growth occurs during the rising part of the stress cycle, rather than at the peak stress. This observation, which has been confirmed by other investigators (58-59), illustrates that time dependent SCC effects often play only a

minor role in FCGR acceleration.

The different theories which describe environmental interactions at the crack tip can be grouped into three general classes (6):

- 1) theories involving the dissolution of metal at the crack tip,
- 2) theories involving mechanical crack tip effects due to oxide formation and repair
- 3) theories involving changes in the local deformation character of the material at the crack tip.

Ford and Hoar (60) have proposed that accelerated FCGR in Al-Mg-Zn alloys in chloride and sulfate solutions can be entirely accounted for by the amount of metal dissolved electrochemically at the crack tip. The extremely high local current transients that they have measured in a scratching electrode test support this mechanism. However, this phenomenon may be simply a superposition of SCC, for Engseth and Scully (61) have proposed a similar mechanism to explain stress corrosion crack growth in stainless steel, and Ford and Hoar themselves have proposed the same mechanism to account for both corrosion fatigue and SCC.

The effect of aqueous environments on the ductility of oxide layers has been demonstrated by Grosskreutz (29). Bradhurst and Leach (26) have shown that the mechanical properties of oxides are dependent on their thickness, which will certainly be affected by the environment. Since most metals, especially aluminum alloys, titanium alloys and stainless steels, will passivate spontaneously when fresh metal is exposed at a crack tip (60-62), the effect of the environment on the oxide will influence subsequent crack growth. If the environment renders the oxide brittle, micro-cracks will form in the oxide during straining which will increase the

local crack tip stress, causing a mechanical increase in crack growth (29). If a thick, more ductile oxide forms, crack growth can be impeded due to crack tip blunting or due to a reduction in ΔK caused by a wedging action of the oxide (63).

Dissolution under strain at a crack tip may change the deformation behavior ahead of the crack tip in the same way that crack initiation is affected by the environment. The repassivation rate of metal at the crack tip can affect plastic deformation either by minimizing the dissolution rate or by affecting slip activity in the fatigue plastic zone. Dawson and Pelloux (52), have used this explanation to account for an observed decrease in growth rate with decreasing frequency for $\alpha - \beta$ titanium alloys in NaCl solution. Fransden et. al. (64) have shown a change in slip mode for a Ni - Cu alloy in hydrogen gas. Gell and Duquette (63) have proposed that formation of a coherent oxide in a planar slip material can disperse slip and reduce crack growth rate. Surface effects discussed by Latanision et. al. (42-44,65) can change the flow behavior of the entire crystal, affecting crack growth. Tyson and Alfred (66) have suggested that adsorption of certain active species at a crack tip can reduce the strength sufficiently to accelerate FCGR through cleavage.

It is likely, however, that in many situations two or three of these mechanisms may operate in tandem to accelerate crack propagation. For 7075-T6 aluminum in 3.5% NaCl, Stoltz and Pelloux (67) have shown changes in striation morphology under applied currents of alternating polarity which cannot be explained on the basis of any single mechanism. These same authors (68) showed that nitrate additions also changed the striation morphology. Furthermore, Misawa, Ringshall, and Knott (56) were unable

to differentiate between a dissolution or adsorption mechanism on the basis of their activation energy measurements for fatigue crack propagation of a low alloy steel in distilled water. Further study is obviously needed to develop methods to differentiate between the various possible mechanisms of corrosion fatigue, both for crack initiation and crack propagation.

B. Metallurgy of Austenitic-Ferritic Stainless Steels

1. Physical Metallurgy

Austenitic-ferritic stainless steels generally contain more than 18% Cr, 4 to 10% Ni, and less than .08% C, along with significant proportions of Mo, Mn, and Si. Cast alloys are generally water quenched from a temperature between 1050°C and 1150°C, which is usually about 200°C below the austenite solvus. The 1100°C isotherm of the Fe-Ni-Cr (69) phase diagram is shown in Figure 3, and the compositions of various commercial alloys are represented on it. By altering the composition and quenching temperature, the volume fraction of austenite can be varied greatly. Figure 4 shows a diagram developed by Schaeffler (70) for stainless steel weld metal, which predicts the metastable volume fraction of each phase, taking into account a wide variety of alloying additions. The austenite stabilizers are grouped together in an expression for nickel equivalent of the form

Nickel equivalent =

$$\%Ni + 30 \times \%C + 0.5 \times \%Mn$$

and plotted against a similar expression for the ferrite stabilizers:

Chromium equivalent =

$$\%Cr + \%Mo + 1.5 \times \%Si + 1.5 \times \%Nb$$

to yield iso-% ferrite lines. Similar diagrams have been developed for

Figure 3: 1100°C isotherm of the Fe-Ni-Cr ternary phase diagram. From ASM Metals Handbook (69). Points indicate composition of various alloys: A) Uranus 50 B) 3RE60 C) Alloy 63 D) VK-A171 E) VK-A271 F) IN-744 G) Type 304 H) Type 430. Dashed line shows position of experimental IN-744 tie-line.

Figure 4: Schaeffler diagram for stainless steel weld metal (70).

wrought stainless steels by Pryce and Andrews (71), and by Giraldenq (72). Jolly (73) has published a diagram plotting % ferrite as a function of the ratio of Cr equivalent/Ni equivalent (Figure 5) and a diagram showing % ferrite as a function of quenching temperature for the alloy Uranus 50 (Figure 6). From these diagrams it is clear that the volume fraction of metastable austenite in the microstructure is very sensitive to composition, quenching temperature, and cooling rate.

Partitioning of the alloying elements between the two phases is significant, and can be predicted from the Fe-Cr-Ni phase diagram for Cr and Ni. Microprobe analysis of the composition of the two phases (73-75) have shown partition ratios (wt. % A in ferrite/wt. % A in austenite) to vary between about 1.8 and 1.2 for ferrite stabilizers and between .35 and .90 for austenite stabilizers.

During slow cooling, lower temperature (<1000°C) heat treatments, or high temperature service, other phase transformations can occur (1,73,74, 76). A chromium-rich ($\approx 45\%$) intermetallic compound known as sigma phase will form as a precipitate at austenite-ferrite phase boundaries and within the ferrite phase between a temperature range of approximately 550°C - 950°C, precipitation being most rapid ($\sim$ minutes) somewhere between 700°C and 900°C, depending on composition. This precipitation can result in localized depletion of chromium in the ferrite, stimulating further ferrite $\rightarrow$ austenite transformation. Precipitation of σ -phase generally increases the hardness of the alloy, producing a corresponding decrease in ductility and corrosion resistance. At somewhat lower temperatures, the formation of a fine intermetallic precipitate can occur within the ferrite; the maximum rate of precipitation is at approximately 475°C. As substantial hardening

Figure 5: Variation in volume fraction ferrite as a function of alloying elements. From Jolly (73).
 $\text{Cr Eq} = \% \text{Cr} + 2 \times \% \text{Mo} + 1.5 \times \% \text{Si}$
 $\text{Ni Eq} = \% \text{Ni} + \% \text{Cu} + 15 \times \% \text{C} + 15 (\% \text{N} - \% \text{Ti}/3.5)$

Figure 6: Variation in volume fraction ferrite as a function of quenching temperature. From Jolly (73).

and embrittlement is produced, this reaction is known as 475°C embrittlement. Although the actual nature of this precipitate is still controversial, it is now generally agreed to be a Cr-rich ($\approx 80\%$) product of a spinodal decomposition of the ferrite phase, and is therefore referred to as α' . In addition to these intermetallic compounds, a chromium carbide of the form $M_{23}C_6$ will precipitate extremely rapidly at the phase boundaries at certain temperatures below 1000°C. This carbide formation, which depletes the region adjacent to the phase boundaries of chromium, is known as sensitization.

Austenitic stainless steels are known to undergo both spontaneous and strain-induced martensitic transformations if the temperature is lowered sufficiently (74,77). For an 18Cr - 12Ni stainless steel, Lecroisey and Pineau (77) found the highest temperature at which martensite will form during deformation, designated the M_d temperature, to be 50°C, while the maximum temperature at which the martensite will form spontaneously, the M_s temperature, is -65°C. This martensite formation was shown to greatly affect subsequent deformation behavior. However, Wakasa and Nakamura (78) have recently shown for an austenitic-ferritic stainless steel that $M_d = -22^\circ\text{C}$ and $M_s = -196^\circ\text{C}$, indicating that no martensite will form during room temperature deformation.

2. Corrosion and Stress Corrosion Cracking Behavior

Early studies of austenitic-ferritic stainless steels centered around their corrosion and SCC resistance, as they were primary candidate materials for use in the chemical industry. In weakly oxidizing acidic environments, the presence of increasing amounts of ferrite improves corrosion resistance, as the polarization between the austenite and ferrite

improves the stability of the passive film (1,79). However, in strongly oxidizing environments, where passivation will not occur, the presence of ferrite detracts from the corrosion resistance, as galvanic action between the two phases can bring about rapid disintegration (79).

SCC in duplex stainless steels can be both intergranular (IG) and transgranular (TG). IGSCC occurs primarily along austenite-ferrite phase boundaries, and is therefore closely related to intergranular corrosion resistance. The precipitation of intermetallic second phases or chromium carbides along boundaries generally accelerates intergranular corrosion, and correspondingly causes susceptibility to IGSCC (80). However, Tedmon and Vermilyea (81) have shown that when sensitization occurs during slow cooling, further cooling following carbide formation will cause the austenite-ferrite boundary to migrate away from the chromium-depleted region due to growth of the austenite islands, because the stable volume fraction of austenite increases as the temperature is lowered. This phenomena prevents sensitization from seriously reducing the intergranular corrosion and IGSCC resistance of duplex stainless steels subjected to slow cooling. Sensitization is still a problem during high temperature service where the boundaries do not migrate.

There is little correlation between IGSCC and TGSCC resistance in commercial alloys. Uranus 50 has been found to be resistant to both forms of SCC, while 3RE60 has been found to be resistant to IGSCC but susceptible to TGSCC (82). Shimodaira et. al. (83) showed that TGSCC will occur in all duplex stainless steels, both austenitic-base and ferritic-base, if the applied stress is high enough. Other studies are contained in recent symposium volumes (84,85,86).

The effect of volume fraction ferrite on SCC resistance has been studied by Flowers, Beck, and Fontana (1) who found ferrite to be beneficial to SCC resistance in commercial alloys up to about a 50% volume fraction, except for high carbon ($\geq 0.08\%C$), non-stabilized alloys. The increased resistance imparted by the ferrite was attributed to a "keying effect" of the ferrite in crack propagation, in which cracks would propagate around rather than through ferrite islands. Shimodaira et. al. (83) also observed this effect, describing it as being both electrochemical and mechanical in nature for ferrite in an austenite matrix. However, for austenite in a ferrite matrix, the keying effect is purely mechanical, for the presence of austenite in a ferrite matrix promotes crack propagation electrochemically. The keying effect is also limited to lower levels of applied stress, for at higher stresses the second phase will fail mechanically and transgranular cracks will link up along the phase boundaries. When the volume fraction of ferrite is varied by changing the nickel content, these authors found a maximum in SCC resistance for an alloy containing 40% ferrite. Their study is somewhat more useful than that of Flowers, Beck and Fontana (1), for the deformation behavior of each phase, as determined by the stacking fault energy (SFE), is much more uniform when only one alloying element is varied.

3. Fatigue and Corrosion Fatigue Behavior

The first study of the fatigue behavior of austenitic-ferritic stainless steels was done by Hayden and Floreen (87) for an $\alpha - \gamma$ alloy series which included the microduplex alloy IN-744. By varying the percentage of each alloying element along an Fe-Ni-Cr phase diagram tie-line, they were able to produce a series of duplex alloys containing

different volume fractions of austenite and ferrite with constant austenite and ferrite composition. This approach eliminates differences in the deformation behavior of the individual phases. The alloys tested by Hayden and Floreen, which contained from 0 to 100% ferrite, displayed a maximum fatigue resistance at 57% ferrite, as shown in Figure 7.

Studies of commercial alloys have produced varying results. Lemaignan (88) showed a slight acceleration of the FCGR at low ΔK for IN-744 in 3.5% NaCl compared to air. Kelley et. al. (2) showed no acceleration of FCGR in a number of cast duplex alloys at a frequency of 10 cps in a simulated paper mill white water solution. Similar results were shown by Liljas and Fridberg (4) for wrought alloy 3RE60. However, Moskovitz (34) found that the fatigue life of both cast and wrought duplex stainless steels was reduced by this solution at 30 cps, and concluded that this effect was due to accelerated crack initiation by a mechanism of enhanced PSB development. Liljas (89) has shown only a slight reduction in the corrosion fatigue resistance of 3RE60 due to sigma phase formation during slow cooling, and no accompanying change in crack propagation mode. This reduction in fatigue resistance is purely a mechanical effect, due to the brittle sigma phase, as no electrochemical acceleration was observed. The lack of electrochemical effect is likely due to the migration of phase boundaries during slow cooling observed by Tedmon and Vermilyea (81), as previously discussed.

As no study on the effect of ferrite fraction on corrosion fatigue similar to that of Hayden and Floreen (75) has been performed to date, a central goal of this investigation is to extend the work of Hayden and Floreen to include the effect of a corrosive environment on the fatigue

Figure 7: Dependence of fatigue limit on volume fraction ferrite, IN-744 tie-line series, from Hayden and Floreen (87).

behavior of different $\alpha - \gamma$ alloy compositions along a tie-line of the Fe-Cr-Ni phase diagram.

III. MATERIALS AND TEST PROCEDURES

A. Description of Alloys

This investigation evaluates the corrosion fatigue behavior of both cast and wrought austenitic-ferritic stainless steels. Three commercially available alloys were studied, designated VK-A171, VK-A271, and Uranus 50. VK-A171 and VK-A271 were supplied in the as-cast condition, water quenched from 1050°C, courtesy of Kubota, Ltd. of Japan and Valmet Oy of Finland. Uranus 50 was supplied in the wrought condition, hot rolled at 1150°C, courtesy of Creusot-Loire of France. The compositions of these commercial alloys are given in Table 1a). Figures 8-10 show the microstructure of these alloys, etched with Kallings' reagent. VK-A171 and VK-A271 contain 50% and 70% ferrite, respectively. Wrought Uranus 50 contains about 40% ferrite and has a much finer distribution of phases than in the cast alloys, with the microstructure elongated in the rolling direction. The mechanical properties of these alloys are given in Table 2.

Five experimental alloys containing from 6% - 100% ferrite were prepared by the General Electric Corporate Research and Development Center. These alloys were hot rolled at 927°C after casting and forging. The composition of these alloys lie along the IN-744 tie-line on the Fe-Ni-Cr phase diagram, as determined by Hayden and Floreen (75), so that the austenite and ferrite phases are of non-varying composition throughout the series of alloys. The composition of these alloys, along with their volume fraction ferrite as determined by a square-counting method, are given in Table 1b). Microstructures are shown in Figures 11-15, revealed by the etchants described in the figure captions.

TABLE 1: COMPOSITION OF ALLOYS

a) COMMERCIAL ALLOYS

<u>ALLOY</u>	<u>C</u>	<u>Cr</u>	<u>Ni</u>	<u>Mo</u>	<u>Mn</u>	<u>Si</u>	<u>P</u>	<u>S</u>	<u>Cu</u>	<u>Ti</u>
VK-A171	.07	22.2	8.3	1.2	.76	1.1	.02	.031	1.6	.08
VK-A271	.06	24.6	4.3	.68	.71	1.3	.02	.02	-	-
Uranus 50	.02	21.4	6.6	2.4	1.9	.55	-	-	-	-

b) IN-744 Tie-Line Series ALLOYS

<u>Heat No.</u>	<u>% Ferrite</u>	<u>C</u>	<u>Cr</u>	<u>Ni</u>	<u>Si</u>	<u>Mn</u>
224	100	.02	31.8	3.2	0.4	0.4
225	79	.02	28.9	4.8	0.4	0.4
226	64	.02	25.2	5.8	0.4	0.4
227	34	.02	21.9	7.6	0.4	0.4
229	6	.02	19.5	8.8	0.4	0.4

TABLE 2
MECHANICAL PROPERTIES OF COMMERCIAL ALLOYS

<u>Alloy</u>	Yield Strength,		UTS,		<u>Elong %</u>	<u>Ref</u>
	<u>MPa</u>	<u>(KSI)</u>	<u>MPa</u>	<u>(KSI)</u>		
VK-A171	379.2	(55.0)	630.2	(91.4)	36.4	2
VK-A271	511.6	(74.2)	643.3	(92.0)	25.6	2
Uranus 50	400.0	(58.0)	670.0	(97.2)	35.0	73

Figure 8: Microstructure of cast alloy VK-A171. Austenite (light) in ferrite (dark) matrix. Kalling's reagent. 100x.

Figure 9: Microstructure of cast alloy VK-A271. Austenite (dark) in ferrite (light) matrix. Kalling's reagent. 100x.

Figure 10: Microstructure of wrought alloy Uranus 50 in the rolling plane. Austenite (light) and ferrite (dark) phases elongated in the rolling direction as indicated by the arrow. 1000x.

Figure 11: Microstructure of Heat 224, 100% ferrite.
Kalling's reagent. 50x.

Figure 12: Microstructure of Heat 225, 79% ferrite.
Austenite islands (light) in ferrite matrix.
17% HNO_3 , 33% HCl , 50% H_2O . 500x.

Figure 13: Microstructure of Heat 226, 64% ferrite.
Austenite islands (light) in ferrite matrix.
17% HNO_3 , 33% HCl , 50% H_2O . 500x.

Figure 14: Microstructure of Heat 227, 34% ferrite.
Bimodal distribution of austenite (light)
with ferrite. Kalling's reagent. 500x.

a) 9% perchloric acid, 45% acetic acid, 46% butylcellosolve, electrolytic etch, 200x.

b) Etched to reveal austenite grain size. 17% HNO_3 , 33% HCl , 50% H_2O , 200x.

Figure 15: Microstructure of Heat 229, 6% ferrite.
Ferrite islands (dark) in austenite matrix.

B. Tensile Tests

Tensile tests were performed on the IN-744 tie-line series alloys to determine yield strength, ultimate tensile strength (UTS), and elongation to fracture. Standard ASTM specifications (90) were followed for specimen geometry and procedure. Tests were carried out on an Instron tensile machine at a crosshead displacement rate of 0.02 in/min (0.05 cm/min), using a longitudinal displacement gage to measure elongation. Specimens were tested in both transverse and longitudinal orientations.

C. Fatigue Crack Growth Rate Tests

Fatigue crack growth rate tests were performed on an MTS servo-controlled hydraulic fatigue machine. Crack length was monitored using a 30x Gaertner traveling microscope. All tests were conducted in tension-tension using a sinusoidal wave form at a frequency of 10 cps. Tests were performed both in lab air and in a simulated paper mill white water solution, consisting of .165% NaCl and .350% Na_2SO_4 in distilled water, adjusted to a pH of 3.5 with H_2SO_4 . This solution was recirculated from a 4 liter reservoir at an approximate flow rate of 2 liters/min through a plexiglass chamber surrounding the crack growth region of the specimen. Cracks were initiated at a stress corresponding to a ΔK value higher than ΔK_{th} , with the stress then being lowered stepwise to the desired level.

Alloy VK-A271 was tested at a stress ratio ($\sigma_{min}/\sigma_{max}$) of $R = 0.6$, to compare with the data of Kelley et. al. (2) at $R = 0.05$. The double cantilever beam (DCB) specimen geometry was used, as shown in Figure 16, with the alternating stress intensity factor at the crack tip given by the equation (91):

NOTE: (1) All dimensions expressed in mm

(2) Tolerances = ± 0.1 mm

Figure 16: Double cantilever beam (DCB) fatigue crack propagation specimen.

$$\Delta K = \Delta \sigma \sqrt{a} [29.6 - 185.0 (a/w) + 655.7 (a/w)^2 - 1017 (a/w)^3 + 638.9 (a/w)^4]$$

where a is the crack length and w the effective specimen width, as shown in Figure 16. $\Delta \sigma = \Delta P/Bw$, where ΔP is the load range and B is the specimen thickness.

Uranus 50 was tested at $R = 0.05$, both in the RW and WR orientations (the first letter indicates direction of load, the second direction of crack growth, R = longitudinal, W = transverse), to investigate the effect of specimen orientation on corrosion fatigue crack growth. The single edge notch (SEN) specimen geometry described by Baratta et. al. (92) was used, as shown in Figure 17, with ΔK at the crack tip given by:

$$\Delta K = \Delta \sigma \sqrt{a} [1.986 + 1.782 (a/w) + 6.998 (a/w)^2 - 21.505 (a/w)^3 + 45.351 (a/w)^4]$$

with a and w as shown in Figure 17.

The five experimental IN-744 tie-line series alloys were tested both at $R = 0.05$ and $R = 0.6$, in the RW orientation only. The SEN specimen geometry was used.

D. Smooth Bar S-N Tests

Stress versus cycles to failure (S-N) tests were conducted on the five IN-744 tie-line series alloys, in lab air and in white water. The tests were performed on Sonntag SF-2U fatigue machines, in fully reversed bending ($R = -1$), at 30 cps. The bending fatigue specimens, shown in Figure 18, were mechanically polished and then electropolished in the reduced section so that subsequent metallographic observations could be

Figure 17: Single-edge-notch (SEN) fatigue crack propagation specimen.

Figure 18: Bending fatigue specimen.

made. The electropolishing solution, which produced a lightly etched surface, consisted of 9% perchloric acid, 45% acetic acid, and 46% butylcellosolve. A potential of 35 volts was used and solution temperature was about 10°C. The maximum stress in the reduced zone of the specimens is determined from the applied load P, by

$$\sigma_{ALT} = \frac{PL t/2}{I}, \quad I = \frac{wt^3}{12}$$

where w is the width of the reduced section, t the specimen thickness, and L the length of the bending moment arm. The white water solution was recirculated around the reduced zone of the specimen through 1/2" ID tygon tubing, as previously described. Tests were run at 52,000 PSI (358.5 MPa), 55,000 PSI (379.2 MPa), and 60,000 PSI (413.7 MPa). Tests were terminated after 8×10^6 cycles if failure had not yet occurred. The specimens were orientated with the specimen axis in the rolling direction and crack growth in the transverse direction, equivalent to the RW orientation described previously.

E. Notched Bar S-N Tests

Stress versus cycles to failure tests were conducted on notched bars of cast alloys VK-A171 and VK-A271, in air and white water solution. The tests were performed on the MTS machine, in tension-tension at 10 cps, using a sinusoidal waveform with stress ratios of $R = 0.05$ and $R = 0.6$. The specimen geometry is shown in Figure 19. Specimens were machined from castings, with the final V-notch machined to a depth of 1.0 mm using a 0.15 mm thick circular jewelers saw. The number of cycles to initiate a crack of length 0.1 mm from the notch was monitored with a 30x Gaertner

Figure 19: Notched bar S-N fatigue specimen.

traveling microscope. The specimens were then cycled to failure. The white water solution was recirculated around the specimens through a plexiglas chamber as previously described.

F. Abrading Electrode Tests

A study was undertaken to model the electrochemical action at an opening fatigue crack tip in an aqueous chloride solution for wrought duplex stainless steels. Electrodes encased in Buehler epoxide mounts were prepared metallographically, with insulated wires emerging from the back of the mount. One electrode was a specimen of the pure ferrite alloy (Heat 224), the other electrode was of the 94% austenite alloy (Heat 229). Each electrode surface was 0.12" x 0.20" (3.0 mm x 5.0 mm). Details of the electrode are shown in Figure 20. A cylindrical plexiglas test chamber was constructed as shown in Figure 21. The electrodes enter the chamber from each side, with the electrode surfaces opposite each other and parallel. In this configuration the electrodes are facing one another during simultaneous abrading by a rotating tool. The plexiglas sleeve also houses a agar-KCl Luggin capillary bridge. This electrically conducting bridge consists of a mixture of saturated KCl solution mixed with 4 gms. of laboratory grade agar per 100 ml KCl, drawn into .066" ID polyethylene intravenous tubing at 70°C. This bridge runs from within 2 mm of the surface of one electrode to an adjacent 100 ml beaker containing a saturated calomel electrode (SCE). Through this bridge the potential of the pure ferrite electrode was measured relative to the SCE by a Wenking potentiostat, and monitored continuously on one channel of a Hewlett-Packard 2-Pen Strip chart recorder. The potential difference

Figure 20: Design of electrode used in abrading electrode experiments.

Figure 21: Apparatus used in abrading electrode experiments.

between the 100% ferrite electrode and the 94% austenite electrode was monitored on the other channel. Both the chamber and the adjacent beaker were filled with 3.5% NaCl solution.

A cylindrical emery grinding wheel was used to abrade the entire surface of both electrodes simultaneously, or each separately. The wheel enters the plexiglas sleeve through a hole in top, and is attached to a Dremel Moto-Tool by metal rod coated with RTV Silicone Sealant. The Moto-Tool is held by a flask clamp supported by a ring stand above the chamber, which is held in place by a large hose clamp attached to the ring stand. The speed of the Moto-Tool is controlled by a Variac autotransformer to drive the 5/8" diameter wheel at 5,000 rpm.

Experiments were conducted in which only the austenite electrode and only the ferrite electrode were abraded, and in which both electrodes were abraded simultaneously. During and following abrasion, the potential of the ferrite electrode versus the SCE and versus the austenite electrode were monitored until they reached constant values. The potential of the austenite electrode versus the SCE was calculated from the other two potentials, as the three potentials must sum to zero.

G. Creep Tests Under Anodic Dissolution

Constant load creep tests were conducted on .61 mm (0.24") diameter annealed type 310 stainless steel wire undergoing anodic dissolution using the apparatus shown in Figure 22. This apparatus is identical to that used by Uhlig (45). Stress was applied by loading weights into a pan attached by a lever arm to the grips holding the wire. Elongation of the wire was determined by a Sanborn DC LVDT transducer which measured displacement of the lever arm, with its output monitored by a strip chart

Figure 22: Creep testing apparatus.

recorder. A plexiglas cylinder 35 cm in diameter fitted with a cylindrical platinum counter electrode surrounded the lower portion of the wire. The cylinder was sealed at the bottom by a rubber stopper with a Teflon insert through which the wire passed. For tests performed below room temperature, a double walled cylinder was used with ice water circulating around the inner cylinder. The electrochemical potential of the wire specimen versus the SCE was monitored by a Wenking potentiostat with a Luggin capillary bridge running from the wire surface to an adjacent beaker containing the SCE.

Two sets of creep tests were run, in which elongation was continuously measured as a function of time. The first set was run in 30% $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ solution, at 23°C and 12°C ($\pm 1^\circ\text{C}$), using nominal stress levels of 275.8 MPa (40 Ksi) and 322.4 MPa (46.75 Ksi). All tests in this solution were run under current control, with anodic current supplied to the wire from a Heathkit current regulating power supply, and measured with a Simpson milliammeter. Dissolution currents ranging from 8.8 mA/cm^2 to 26.9 mA/cm^2 were applied, occasionally interspersed with periods of no applied current. The time at each current value and at zero current were determined by the time required for the specimen to attain a constant creep rate. The second set of experiments was conducted similarly, in $5\text{N H}_2\text{SO}_4 + .5\text{N NaCl}$ solution, at 23°C and 12°C ($\pm 1^\circ\text{C}$), using a nominal stress level of 322.4 MPa (46.75 Ksi). All tests in this solution were performed under potentiostatic control using a Wenking potentiostat. The applied anodic current was recorded on a two-pen strip chart recorder along with the LVDT output. Applied potentials in the active range producing currents from $.002 \text{ mA/cm}^2$ to 6 mA/cm^2 were used. For the first

set of tests, the creep rate was normalized to account for the increase in applied stress caused by a decrease in wire diameter due to electrochemical dissolution. This effect was negligible for the second set of tests due to the use of much lower anodic currents. Creep rates for zero applied current were measured at the conclusion of the tests, generally over a 12 hour period.

H. Anodic Polarization Curves

Anodic polarization diagrams were generated for the experimental duplex alloys of Heat 224 (100% ferrite) and Heat 229 (94% austenite) in 3.5% NaCl solution at room temperature. The basic principles of anodic polarization diagrams are discussed by many authors (93-97). Experiments were performed in the specimen chamber used for the abrading electrode tests in the same configuration, except that one electrode was replaced with a platinum counter electrode. Applied potential was controlled by a Wenking potentiostat. Potential was increased from the rest potential in a stepwise fashion, at the rate of 25 mV every two minutes. Anodic current was recorded at the end of each two minute interval.

Polarization diagrams were also generated for the type 310 stainless steel used in the creep tests in the 5N H_2SO_4 + .5N NaCl solution, at 23°C and 12°C ($\pm 1^\circ\text{C}$), for the active region only. These tests were performed in the creep testing apparatus under no load.

I. Fractography

Fracture surfaces from all FCGR tests were examined in a Cambridge Mark II Stereoscan scanning electron microscope (SEM). The specimens were coated with approximately 200 Å of gold before examination. For the cast duplex alloys, the microstructural phases were identified by EDAX energy

dispersive X-ray analysis.

The electropolished surfaces of the smooth bar bending fatigue specimens were examined in the SEM in order to observe the nature of the surface deformation and crack initiation.

IV. RESULTS

A. Tensile Tests

The tensile data determined for the experimental IN-744 tie-line series alloys is shown in Figure 23. This figure presents the 0.2% offset yield strength, ultimate tensile strength (UTS), and elongation to fracture as a function of volume fraction ferrite, for both longitudinal and transverse orientations. The following features are observed:

- The yield strength increases and the elongation decreases with increasing ferrite fraction up to about 65%.
- The UTS varies only slightly with ferrite fraction, showing no particular trend.
- The alloys are slightly stronger and less ductile in the transverse direction, as compared to the longitudinal direction.

B. Fatigue Crack Growth Rate Tests

1. Commercial Alloys

The fatigue crack growth rates for VK-A271 are plotted as a function of ΔK in Figure 24. Data is given for crack propagation in air and in white water at $R = 0.6$, and referenced to the dashed line, which is the FCGR data determined by Kelley et. al. (2) for $R = 0.05$, independent of environment. The following observations can be made from this data:

- FCGR is increased by an increase in R , regardless of ΔK level or environment.
- ΔK_{th} is lowered by an increase in R .
- The effect of a corrosive environment at $R = 0.6$ is apparent

Figure 23: Dependence of tensile properties on volume fraction ferrite for the IN-744 tie-line series alloys.

Figure 24: Fatigue crack growth rate curves, VK-A271, showing effect of stress ratio. Dashed line from Kelley et. al. (2).

in a lowering of ΔK_{th} relative to air and an increase in FCGR at low ΔK values, in contrast to the lack of environmental effects observed by Kelley et. al. at $R = 0.05$. The FCGR curves for air and white water at $R = 0.6$ converge at high ΔK values.

The FCGR curves for Uranus 50 at $R = 0.05$ are plotted in Figure 25. Data is given for both the WR and RW orientations, in air and in white water. The FCGR for the RW specimens are slightly lower than for the WR specimens, with little change in ΔK_{th} . The only observable environmental effects are at low ΔK , for which there is a slight acceleration of FCGR in white water at growth rates between 10^{-6} and 4×10^{-6} in/cycle (2.5×10^{-8} and 10^{-7} m/cycle).

2. Tie-Line Series Alloys

The FCGR curves for the experimental IN-744 tie-line series of alloys are plotted in Figures 26-34. Figures 26-30 give data for each of the five alloys, in air and white water, at $R = 0.05$ and $R = 0.6$. Figures 31-34 compare the five alloys under each combination of environment and mean stress. Figure 35 shows the dependence of ΔK_{th} on volume fraction ferrite, with the ΔK_{th} values determined from the FCGR curves. Figures 36 and 37 show the ΔK values required to produce FCGR of 5×10^{-6} in/cycle (1.25×10^{-7} m/cycle) and 5×10^{-5} in/cycle (1.25×10^{-6} m/cycle) respectively. The following observations can be made from this data:

- At $R = 0.05$, ΔK_{th} is highest both in air and white water for Heat 226, which contains 64% ferrite. At $R = 0.6$, ΔK_{th} is highest in air for Heat 226 (64% ferrite), but is highest in white water for Heat 225 (79% ferrite).

Figure 25: Fatigue crack growth rate curves, Uranus 50, showing effect of specimen orientation. Transverse = RW, Longitudinal = WR.

Figure 26: Fatigue crack growth rate curves, Heat 224.

Figure 27: Fatigue crack growth rate curves, Heat 225.

Figure 28: Fatigue crack growth rate curves, Heat 226.

Figure 29: Fatigue crack growth rate curves, Heat 227.

Figure 30: Fatigue crack growth rate curves, Heat 229.

Figure 31: Fatigue crack growth rate curves, tie-line series alloys, air, $R = 0.05$.

Figure 32: Fatigue crack growth rate curves, tie-line series alloys, white water, R = 0.05.

Figure 33: Fatigue crack growth rate curves, tie-line series alloys, air, R = 0.6.

Figure 34: Fatigue crack growth rate curves, tie-line series alloys, white water, R = 0.6.

Figure 35: Dependence of ΔK_{th} on volume fraction ferrite for the tie-line series alloys.

Figure 36: Dependence of ΔK required to cause a crack growth rate of 5×10^{-6} in/cycle (1.25×10^{-7} m/cycle) on volume fraction ferrite for the tie-line series alloys.

Figure 37: Dependence of ΔK required to cause a crack growth rate of 5×10^{-5} in/cycle (1.25×10^{-6} m/cycle) on volume fraction ferrite for the tie-line series alloys.

- At $R = 0.05$, environmental reduction of ΔK_{th} and acceleration of FCGR at low ΔK are greatest for Heat 225 (79% ferrite), followed by Heat 226 (64% ferrite). These environmental effects disappear as ΔK increases. Environmental effects are negligible for Heat 224 (94% austenite), 225 (66% austenite), and 229 (100% ferrite).

- At $R = 0.6$, environmental reduction of ΔK_{th} and acceleration of FCGR at low ΔK increase with increasing volume fraction of austenite. These environmental effects also disappear as ΔK increases.

- The effect of stress ratio, R , on ΔK_{th} and low- ΔK FCGR in air is greatest for Heats 225 (79% ferrite) and 226 (64% ferrite), which have the highest ΔK_{th} values. In white water, the effect of R is dependent on environmental sensitivities. At high ΔK , independent of environment, the acceleration of FCGR with increasing R is about the same for all five alloys.

- At high ΔK , FCGR decreases with increasing % ferrite up to 64% ferrite, where it becomes constant. At high ΔK , all FCGR are independent of environment.

C. Smooth Bar S-N Tests

Results of the smooth bar bending fatigue tests on the tie-line series alloys in air and white water are given in Figures 38-40. These figures show the number of cycles to failure versus ferrite content for alternating stress levels of 52,000 PSI (358.5 MPa), 55,000 PSI (379.2 MPa), and 60,000 PSI (413.7 MPa), respectively.

Heat 226 (64% ferrite) exhibits the longest lifetimes at all stress levels, both in air and white water, with lifetime decreasing continuously with both increasing and decreasing ferrite content away from this

Figure 38: Dependence of fatigue lifetime on volume fraction ferrite for the tie-line series alloys, at an alternating stress level of 52,000 PSI (358.5 MPa) in fully reversed bending.

Figure 39: Dependence of fatigue lifetime on volume fraction ferrite for the tie-line series alloys, at an alternating stress level of 55,000 PSI (379.2 MPa) in fully reversed bending.

Figure 40: Dependence of fatigue lifetime on volume fraction ferrite for the tie-line series alloys, at an alternating stress level of 60,000 PSI (413.7 MPa) in fully reversed bending.

maximum. There is one exception; at 60,000 PSI, Heat 225 (79% ferrite) has a greater lifetime in white water. In all cases, the 100% ferrite alloy exhibited greater lifetimes than the 94% austenite alloy. The white water environment did reduce the lifetime of the Heat 224 (100% ferrite) in contrast to its lack of influence on FCGR. The effect of the environment on the lifetime of the 94% austenite alloy depends on stress level. At a stress level of 52,000 PSI, close to the fatigue limit (8×10^5 cycles at 50,000 PSI (344.7 MPa) in air did not cause failure), the white water accelerated failure significantly. However, at higher stress levels, the white water actually retarded failure. For the other alloys, environmental acceleration of failure was significant at the lower stress levels, but became negligible at 60,000 PSI (413.7 MPa) except for Heat 226 (64% ferrite).

D. Notched Bar S-N Tests

Results of the notched bar fatigue tests for commercial alloy VK-A271 are shown in Figure 41. This figure shows stress versus cycles to initiation and cycles to failure data in air and white water, at $R = 0.05$ and $R = 0.6$. Curves are drawn only for the data points representing failure. Data points for alloy VK-A171 are omitted for clarity, but in all cases they fell within the scatterbands for VK-A271. The white water solution significantly lowered the number of cycles required for crack initiation from a notch at $R = 0.05$, but had little effect at $R = 0.6$. However, by increasing R from 0.05 to 0.6, i.e. superimposing a high mean tensile stress on the sinusoidal cyclic loading, the time required to initiate a crack and the subsequent time to failure were both greatly reduced for a given alternating stress. The fatigue limits obtained from the S-N

Figure 41: Notched bar S-N data, VK-A271. Curves drawn for failure only.

curves in Figure 41 can be converted to ΔK_{th} values, according to the expression

$$\Delta K_{th} = 1.1 \Delta \sigma_L \sqrt{\pi a}$$

where $\Delta \sigma_L$ is the fatigue limit, and a is the initial notch depth (1.00mm).

The values of ΔK_{th} thus obtained are: 9.9 KSI $\sqrt{in}$ (10.9 MPa $\sqrt{m}$) in air at $R = 0.05$; 8.0 KSI $\sqrt{in}$ (8.8 MPa $\sqrt{m}$) in white water at $R = 0.05$; and 6.3 KSI $\sqrt{m}$ (6.9 MPa $\sqrt{m}$) in air and in white water at $R = 0.6$.

E. Abrading Electrode Tests

Results of the abrading electrode tests are presented in Figures 42-44. These figures contain plots of electrochemical potential in 3.5% NaCl solution as a function of time between ferrite and austenite (94%), ferrite and the SCE, and austenite and the SCE. Figure 42 gives these curves for the case where both electrodes were abraded simultaneously. During abrasion, the austenite is slightly anodic to the ferrite. Following abrasion, the ferrite repassivates more rapidly than the austenite, resulting in the potential difference between the two being a maximum after 4 seconds. Subsequently, the potential difference falls back to the steady state rest potential difference of about 70 mV. Figure 43 gives the curves for the case where only the ferrite is abraded. During abrasion, the ferrite is highly anodic to the passivated austenite, and has the effect of polarizing the austenite about 350 mV from its rest potential in the noble direction. Following abrasion, the potential difference between the austenite and ferrite falls off rapidly, as the ferrite repassivates and the austenite simultaneously depolarizes, with the austenite eventually becoming anodic to the ferrite after about 500

Figure 42: Abrading electrode test data. Change in electrochemical potentials with time after both electrodes were abraded.

Figure 43: Abrading electrode test data. Change in electrochemical potential with time after only the ferrite electrode was abraded.

Figure 44: Abrading electrode test data. Change in electrochemical potential with time after only the austenite electrode was abraded.

seconds.

To aid in interpreting these experiments, the anodic polarization diagrams for Heat 224 (100% ferrite) and Heat 229 (94% austenite) are given in Figure 45. The diagrams show that the current densities at anodic potentials are much greater for austenite than for ferrite. The ferrite shows a defined passive region with accompanying low current densities, and does not exhibit high current densities until transpassive potentials are reached. In contrast, the austenite undergoes a transition to pitting with accompanying high current densities at a much lower potential.

F. Creep Tests Under Anodic Dissolution

The results of the creep tests performed under anodic dissolution for type 310 stainless steel wire in 30% $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ solution are given in Figures 46 and 47. Figure 46 shows the creep elongation vs. time data under various applied current densities in a typical test. The curves in Figure 47 plot creep rate as a function of applied anodic current density at 23°C ($\pm 1^\circ\text{C}$) and 12°C ($\pm 1^\circ\text{C}$) for nominal applied stress levels of 40,000 PSI (275.8 MPa) and 46,750 PSI (322.4 MPa). The electrochemical potential during these tests was around +1100 mV vs. SCE. The following features can be observed from these curves:

- Creep rate increases continuously with increasing current density.
- Creep rate increases with increasing stress.
- Creep rate increases with decreasing temperature.
- The acceleration of creep rate under anodic dissolution is not due to a reduction in the cross-sectional area of the wire, because creep

Figure 45: Anodic polarization diagrams in 3.5% NaCl for Heat 224 (100% ferrite) and Heat 229 (94% austenite).

Figure 46: Typical curve of creep elongation as a function of time for various applied anodic current densities. 310 Stainless steel wire in a 30% $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ solution at 12°C. Applied stress is 46,750 PSI (322.4 MPa).

Figure 47: Dependence of creep rate on anodic current density for 310 stainless steel in 30% $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ solution.

rates for zero current were determined at the end of the tests for wires with reduced cross-sections, and the data in Figure 47 was normalized to account for this reduction. (See Appendix.)

Figure 48 shows SEM micrographs of the wire surface after dissolution-induced creep. These micrographs show that the surface attack consists of fairly uniform pitting which results in a uniform reduction in cross-sectional area.

Figure 49 shows the creep rate as a function of current density in 5N H₂SO₄ + .5N NaCl solution, at 23°C and 12°C, for a nominal applied stress level of 46,750 PSI (322.4 MPa). The applied anodic currents were generated under potentiostatic polarization within the active range. The anodic polarization curves for the 310 stainless steel wire in 5N H₂SO₄ + .5N NaCl solution at 23°C and 12°C are shown in Figure 50. In contrast to the current controlled dissolution in the FeCl₂ solution at potentials around +1100 mV vs. SCE, this potentiostatic controlled dissolution at potentials within the active range (-250 to -100 mV vs. SCE) in the 5N H₂SO₄ + .5N NaCl solution showed no dependence of dissolution enhanced creep rates on temperature, as evidenced in Figure 49. Furthermore, the creep rates at a given current density in the acid solution during active dissolution are greater than the creep rates in the FeCl₂ solution during transpassive dissolution.

G. Fractography

1. Smooth Bar Crack Initiation Surfaces - IN-744 Tie-Line Series Alloys

SEM micrographs of the electropolished smooth bar S-N specimens are presented in Figures 51-55. Crack initiation morphology was observed

a) 140x

b) 700x

Figure 48: SEM micrographs of surface of 310 stainless steel wire following creep test under anodic dissolution in ferrous chloride solution.

Figure 49: Dependence of creep rate on anodic current density for 310 stainless steel in 5N H₂SO₄ + .5N NaCl solution.

Figure 50: Anodic polarization diagrams in the range of active potentials for 310 stainless steel wire in 5N H₂SO₄ + .5N NaCl solution.

to be the same in air and in white water. In the fully ferritic alloy (Heat 224) deformation is concentrated in coarse, widely spaced slip bands leading to crack initiation, often at grain boundaries, as shown in Figure 51. For Heat 225 (79% ferrite), deformation is concentrated in the ferrite phase in much finer slip bands, with many associated microcracks, Figure 52. As the amount of austenite increases further, deformation in the form of fine slip bands and microcracks occurs in both phases, as shown for Heat 226 (64% ferrite) in Figure 53. For the high austenite alloys, Heats 227 (34% ferrite) and 229 (6% ferrite), slip in the austenite is quite heavy with many microcracks, as shown in Figures 54 and 55. Cracking planes are very crystallographic, especially for the 96% austenite alloy.

2. Fracture Surfaces - IN-744 Tie-Line Series Alloys

The fracture surfaces for Heat 224 (100% ferrite) are shown in Figures 56-58. In these and all subsequent fractographs, the direction of crack growth is indicated by the arrow. In air for $R = 0.05$, low- ΔK failure appears fairly ductile (Figure 56). As ΔK increases, ductile striations become observable (Figure 57). In white water for $R = 0.05$, some intergranular fracture is mixed with the ductile features at low ΔK . When R is increased to 0.6, low ΔK failure appears more brittle (Figure 58). At high ΔK all fracture surfaces appear similar, regardless of R ratio or environment.

The fracture surfaces for Heat 225 (79% ferrite) are shown in Figures 59-62. In air at $R = 0.05$, fairly ductile fatigue at low ΔK (Figure 59) gives way to ductile striation formation at high ΔK (Figure 61). In white water at $R = 0.05$, low ΔK fracture surfaces

a) 165x

b) 1650x

Figure 51: Crack initiation at PSB and grain boundaries,
Heat 224. $\sigma_{ALT} = 52,000$ PSI (358.5 MPa).

Figure 52: Crack initiation at PSB in ferrite, Heat 225.
 $\sigma_{ALT} = 60,000 \text{ PSI (413.7 MPa)}$. 1600x.

Figure 53: Crack initiation at PSB in both phases, Heat 226.
 $\sigma_{ALT} = 55,000 \text{ PSI (379.2 MPa)}$. 1600x.

Figure 54: Crack initiation at PSB in austenite, Heat 227. $\sigma_{ALT} = 60,000$ PSI (413.7 MPa). 1500x.

Figure 55: Crack initiation at PSB in austenite, Heat 229. $\sigma_{ALT} = 52,000$ PSI (358.5 MPa). 800x.

a) 150x

b) 750x

Figure 56: Fracture surface, Heat 224, air, $R = 0.05$, $\Delta K = 25 \text{ KSI}\sqrt{\text{m}}$ ($27.5 \text{ MPa}\sqrt{\text{m}}$). Crystallographic pseudo-cleavage with ductile striations.

Figure 57: Fracture surface, Heat 224, air, $R=0.05$, $\Delta K = 37 \text{ KSI}\sqrt{\text{in}}$ ($40.7 \text{ MPa}\sqrt{\text{m}}$). Ductile striations. 750x.

Figure 58: Fracture surface, Heat 224, air, $R = 0.6$, $\Delta K = 16 \text{ KSI}\sqrt{\text{in}}$ ($17.6 \text{ MPa}\sqrt{\text{m}}$). Feathery with elongated plateaus. 750x.

a) 425x

b) 1700x

Figure 59: Fracture surface, Heat 225, air, $R = 0.05$.
 $\Delta K = 23 \text{ KSI}\sqrt{\text{in}}$ ($25.3 \text{ MPa}\sqrt{\text{m}}$). Pseudo-cleavage planes.

a) 425x

b) 1700x

Figure 60: Fracture surface, Heat 225, white water,
 $R = 0.05$, $\Delta K = 19 \text{ KSI}\sqrt{\text{in}}$ ($20.9 \text{ MPa}\sqrt{\text{m}}$).
Dissolution of austenite phase.

Figure 61: Fracture surface, Heat 225, air, $R = 0.05$, $\Delta K = 59 \text{ KSI}\sqrt{\text{in}}$ ($64.9 \text{ MPa}\sqrt{\text{m}}$). Ductile striations. 750x.

Figure 62: Fracture surface, Heat 225, air, $R = 0.6$, $\Delta K = 18.5 \text{ KSI}\sqrt{\text{in}}$ ($20.4 \text{ MPa}\sqrt{\text{m}}$). Ductile striations on small plateaus. 1700x.

contain many corroded regions which show evidence of corrosive attack of the austenite (Figure 60). At $R = 0.6$, the fracture surfaces at low ΔK are much smoother (Figure 62), and show no environmental dependence. At high ΔK , all fracture surfaces appear similar to Figure 61.

The fracture surfaces for Heat 226 (64% ferrite) are mostly similar to those shown for Heat 225, except as described below. Failure in air at $R = 0.05$ appears identical to Figures 60 and 61. At $R = 0.05$ in white water, low- ΔK fracture surfaces show evidence of the corrosion attack observed for Heat 225, as well as some transgranular cleavage-like failure, both of which are observable in Figure 63. At $R = 0.6$, the low- ΔK fracture in air, as shown in Figure 64 a, is much rougher than for Heat 225. In white water, a great deal of secondary cracking with cleavage-like features is exhibited, as shown in Figure 64 b.

The fracture surfaces for Heat 227 (34% ferrite) are shown in Figures 65 and 66. In air, the fracture surfaces show no dependence on R ratio. At low ΔK , the appearance is quite ductile, as shown in Figure 65, leading to ductile striation formation at high ΔK . In white water, Figure 66, low ΔK failure contains some transgranular cleavage-like failure at $R = 0.05$, which is much more evident at $R = 0.6$. All fracture surfaces at high ΔK appear similar, consisting mainly of ductile striations.

The fracture surfaces for Heat 229 (6% ferrite) are shown in Figures 67-70. In air at low ΔK , Figure 67, failure is quite ductile, regardless of R , similar to Heat 227. At higher ΔK , the fracture surface contains ductile striations mixed with dimples, as shown in Figure 68. In white water at low ΔK , transgranular cleavage is very evident

a) 1750x

b) 3750x

Figure 63: Fracture surfaces, Heat 226, white water,
 $R = 0.6$, $\Delta K = 22 \text{ KSI}\sqrt{\text{in}}$ ($24.2 \text{ MPa}\sqrt{\text{m}}$).
Dissolution of austenite with some cleavage.

a) air, $\Delta K = 17.5 \text{ KSI}\sqrt{\text{in}}$ ($19.3 \text{ MPa}\sqrt{\text{m}}$). Elongated plateaus. 1750x.

b) white water, $\Delta K = 16 \text{ KSI}\sqrt{\text{in}}$ ($17.6 \text{ MPa}\sqrt{\text{m}}$). Cleavage with secondary cracks on elongated plateaus. 1600x.

Figure 64: Fracture surfaces, Heat 226, $R = 0.6$.

Figure 65: Fracture surface, Heat 227, air, $R = 0.05$, $\Delta K = 19 \text{ KSI}\sqrt{\text{in}}$ ($20.9 \text{ MPa}\sqrt{\text{m}}$). Feathery ductile features. 1600x.

Figure 66: Fracture surface, Heat 227, white water, $R = 0.6$, $\Delta K = 14 \text{ KSI}\sqrt{\text{in}}$ ($15.4 \text{ MPa}\sqrt{\text{m}}$). Mixed elongated plateaus and cleavage. 800x.

Figure 67: Fracture surface, Heat 229, air, $R = 0.05$, $\Delta K = 19 \text{ KSI}\sqrt{\text{in}}$ ($20.9 \text{ MPa}\sqrt{\text{m}}$). Feathery ductile features. 1600x.

Figure 68: Fracture surface, Heat 229, air, $R = 0.6$, $\Delta K = 30 \text{ KSI}\sqrt{\text{in}}$ ($33.0 \text{ MPa}\sqrt{\text{m}}$). Mixed ductile striations and dimples. 1500x.

Figure 69: Fracture surface, Heat 229, white water, $R = 0.05$, $\Delta K = 21 \text{ KSI}\sqrt{\text{in}}$ ($23.1 \text{ MPa}\sqrt{\text{m}}$). Mixed feathery ductile tears and cleavage. 800x.

Figure 70: Fracture surface, Heat 229, white water, $R = 0.6$, $\Delta K = 14.8 \text{ KSI}\sqrt{\text{in}}$ ($16.3 \text{ MPa}\sqrt{\text{m}}$). Mixed elongated plateaus and cleavage. 750x.

mixed with more ductile features, both at $R = 0.05$, Figure 69, and at $R = 0.6$, Figure 70. At high ΔK , all fracture surfaces appear the same, similar to Figure 68.

Table 3 summarizes the fracture surface features at low ΔK , indicating their dependence on R ratio and environment. At high ΔK , ductile striations were always evident regardless of R ratio or environment, with the addition of dimples for the 94% austenite alloy.

3. Fracture Surfaces - Commercial Alloys

SEM micrographs of fracture surfaces of alloy VK-A271 are presented in Figures 71-73. Figure 71 shows the appearance of fatigue failure at low ΔK for $R = 0.05$, in which the failure in the austenite phase appears similar to that in the ferrite phase. At higher ΔK , Figure 72, fatigue striations are clearly evident. The crack front, as indicated by the position of a single striation, is further ahead in the ferrite than in the austenite, indicating the tendency towards more rapid crack growth in the ferrite. Figure 73 shows the change in fracture mode when R is increased to 0.6. For ferrite grains with the proper orientation, cleavage-like fracture is evident, even at low ΔK , with the accompanying fracture in the austenite appearing much more ductile. For ferrite grains not orientated for cleavage, the fracture in the ferrite still appears much more brittle than the austenite, similar to Figure 71. At higher ΔK , the fracture surfaces appear much the same as at $R = 0.05$. There were no observable environmental effects on the appearance of the fracture surfaces of these alloys.

Figures 74 and 75 show the effect of specimen orientation for wrought Uranus 50. For the RW oriented specimens, there are a large

TABLE 3: SUMMARY OF FRACTURE SURFACES AT LOW ΔK FOR TIE-LINE SERIES ALLOYS

<u>Heat #</u>	<u>% Ferrite</u>	<u>Air, R=0.05</u>	<u>White Water, R=0.05</u>	<u>Air, R=0.6</u>	<u>White Water, R=0.6</u>
224	100	crystallographic (pseudo-cleavage) with ductile striations	crystallographic with ductile striations, some intergranular	feathery with elongated plateaus	feathery with elongated plateaus
225	79	pseudo-cleavage planes with adjacent ductile striations	ductile features with regions of dissolution of austenite	ductile striations on small plateaus	ductile striations on small plateaus
226	64	small crystallographic plateaus with ductile tears	ductile features with regions of dissolution of austenite, some cleavage	elongated plateaus	cleavage with many secondary cracks on elongated plateaus
227	34	feathery ductile features	feathery ductile tears with some cleavage	ductile striations on elongated plateaus	mixed elongated plateaus and cleavage
229	6	feathery ductile features	mixed feathery ductile tears and cleavage	ductile striations on elongated plateaus	mixed elongated plateaus and cleavage

a) 200x

b) 1000x

Figure 71: Fracture surface, VK-A271, $R = 0.05$, low ΔK .
Pseudo-cleavage in ferrite phase.

a) 500x

b) 2000x

Figure 72: Fracture surface, VK-A271, $R = 0.05$, high ΔK .
 * Crack front in austenite trails crack front in ferrite.

a) 85x

b) 425x

Figure 73: Fracture surface, VK-A271, $R = 0.6$, oriented for cleavage in ferrite.

Figure 74: Fracture surface, Uranus 50, RW orientation, $\Delta K = 24 \text{ KSI}\sqrt{\text{in}}$ ($26.4 \text{ MPa}\sqrt{\text{m}}$). Microcracks perpendicular to crack growth direction. 450x.

Figure 75: Fracture surface, Uranus 50, WR orientation, $\Delta K = 19 \text{ KSI}\sqrt{\text{in}}$ ($20.9 \text{ MPa}\sqrt{\text{m}}$). Microcracks and grooves in crack growth direction. 450x.

number of secondary microcracks perpendicular to the crack growth direction, Figure 74. For the WR specimens, Figure 75, there are secondary microcracks and grooves parallel to the crack growth direction. There were no observable environmental effects on the appearance of the fracture surfaces of these alloys.

V. DISCUSSION

This discussion section will deal with two major topics. The first of these is the actual mechanism by which electrochemical dissolution accelerates fatigue crack initiation. The second of these is the effect of microstructure on the corrosion fatigue behavior of austenitic-ferritic stainless steels, and the mechanisms underlying this microstructural dependence.

A. Environmental Acceleration of Fatigue Crack Initiation

In the research program preceding this present work (34), the specific topic of the mechanism of corrosion fatigue crack initiation in cast austenitic-ferritic stainless steels was studied. Observations of crack initiation in commercial alloys showed a definite acceleration of PSB formation in austenite under the influence of electrochemical dissolution, accounting for a shift in crack initiation sites at low stress levels from inclusions and phase boundaries to PSB. Repassivation rate studies as a function of pH supported the theory that the accelerated crack initiation at PSB was caused by enhanced PSB formation due to surface dissolution, rather than by the creation of crack nuclei by dissolution at exposed slip steps where the passive film was ruptured.

This present study offers further data in support of the enhanced PSB formation model of corrosion fatigue crack initiation, in the form of the creep tests performed under anodic dissolution. Previous creep and corrosion fatigue studies of this type performed by Uhlig et. al. (35,37, 45) have suggested various mechanisms by which dissolution can effect surface plasticity. The creep data for 310 stainless steel presented in

section F of the results are similar to the findings of Uhlig et. al. for copper and iron, in that they show a definite increase in creep rate during anodic dissolution. However, they deviate from previous studies in two important aspects. First, the creep rate was shown to be not only a function of current density, but also a function of electrochemical potential and environment. Second, the creep rate was found to be inversely dependent on temperature when dissolution occurred at potentials around +1100 mV vs. SCE in ferrous chloride solution.

The difference in the actual dissolution-induced creep rates and their temperature dependence between the ferrous chloride solution and the sulfuric acid-sodium chloride solution must be due to the following. In the ferrous chloride solution, anodic polarization was galvanostatic and occurred at potentials where both oxide film formation and oxygen evolution can occur. In the sulfuric acid-sodium chloride solution, anodic polarization was potentiostatic and occurred at active potentials, where no films will form and oxygen evolution will not occur. For stainless steel in chloride solutions, the stable species of chromium in equilibrium with the electrolyte above a potential of +1000 mV vs. SCE is the $\text{Cr}_2\text{O}_7^{2-}$ ion (62, 96,97), which is produced by the anodic reactions:

Similar equations can also be written for iron and nickel, which form a mixed metal oxide film along with the chromium. Additionally, because the potential is above the stable potential for water, an anodic oxygen

evolution reaction also occurs:

Therefore, when the current density of the anodic process on the stainless steel wire is controlled externally, the current must be divided between these three possible reactions:

$$i_a = i_1 + i_2 + i_3$$

The anodic oxygen evolution reaction kinetics, analogous to cathodic hydrogen evolution kinetics, are very sensitive to temperature (98). As temperature rises, the reaction rate increases, therefore i_3 increases. From the polarization diagrams in Figure 50, it is evident that the passive current density is higher at higher temperatures. This increased passive current density may indicate that a thicker surface oxide layer is present (62). Therefore, the anodic current going towards Cr_2O_3 formation in reaction 1, designated i_1 , should also increase with temperature. Since the total anodic current, i_a , is being controlled galvanostatically independent of temperature, and the anodic current producing dissolution by reaction 2 is given by

$$i_2 = i_a - (i_1 + i_3),$$

then the dissolution current must decrease with increasing temperature.

The increase in creep rate with decreasing temperature can be due to two possible effects:

- 1) the percentage of current going towards surface dissolution increases with decreasing temperature

- 2) the thickness of the unstable surface oxide may decrease with decreasing temperature.

Either explanation is plausible, and it is conceivable that these two mechanisms may operate in parallel. The theory that the increase in creep rate with decreasing temperature is due simply to an increase in surface dissolution is valid, as dissolution of obstacles to near-surface dislocation motion could certainly occur. This theory has been discussed in relation to corrosion fatigue crack initiation. The theory that this effect could be due to the presence of a thicker oxide at higher temperatures is also valid, for the effect of surface films on near-surface dislocation motion and mechanical properties has also been proven (20-28), although only for surface films much thicker than the oxide films on stainless steels.

During potentiostatically controlled anodic polarization in the sulfuric acid-sodium chloride solution at active potentials, there is only one anodic reaction, which is the dissolution reaction (94):

The entire applied current goes towards dissolution, and there is no oxide present on the surface. The increase in creep rate at constant current density in the sulfuric acid - sodium chloride solution over the ferrous chloride solution and the lack of temperature dependence of creep rate in the sulfuric acid - sodium chloride solution can be due to either of the effects just discussed:

- 1) The entire applied current goes towards dissolution, independent of temperature, in the sulfuric acid - sodium chloride solution,

whereas only a fraction of the applied current goes toward dissolution in the ferrous chloride solution.

2) There is no oxide present on the metal surface in the sulfuric acid -sodium chloride solution, regardless of temperature. There cannot be any decrease in creep rate due to oxide blocking of dislocation motion as in the ferrous chloride solution, nor can there be any temperature dependence due to changes in oxide thickness.

Although there was no acceleration of crack initiation visibly evident on the surface of the smooth bar S-N specimens of the IN-744 tie-line series alloys, there was a definite decrease in time to failure in white water at 52,000 PSI (358.5 MPa) for all five alloys. This acceleration occurred despite the fact that Heats 224, 227, and 229 (100%, 34%, and 6% ferrite, respectively) showed little environmental acceleration of FCGR at $R = 0.05$. The initiation stage therefore must be accelerated by the white water solution in these three alloys. Since initiation in all five alloys was observed to occur at PSB, it follows that the accelerated crack initiation must be due to the acceleration of PSB formation during surface dissolution, or due to the slip-dissolution - reverse slip mechanism of Pyle, Rollins, and Howard (32,33).

The creep data indicates that near-surface plastic deformation is accelerated by electrochemical dissolution at the metal surface. Whether this effect occurs by actual dissolution of dislocation tangles, or due to changes in the thickness of the oxide film is unclear. However, either mechanism can be responsible for an acceleration of PSB formation during cyclic loading, accounting for accelerated crack initiation. There is no need to invoke the mechanism of Pyle, Rollins, and Howard, for it implies

that deformation culminating in PSB formation is unaffected by surface dissolution, and that localized dissolution at PSB is required for environmental acceleration to occur, which is clearly not the case.

These findings are quite compatible with other recent studies on corrosion fatigue crack initiation. Duquette et. al. (41) found a less developed dislocation cell structure in the near-surface regions under the influence of anodic dissolution, which lead to more rapid crack initiation in OFHC copper. It is likely that this poorly developed cell structure is more easily transferable to the ladder structure required for PSB formation, because there are fewer interactions and more matrix dislocations. If the fatigue strain limit for PSB formation described by Laird (15,16) is that strain required to produce the transition to the ladder structure, then when surface dissolution produces a less-developed, more easily transferable cell structure, the fatigue limit will obviously be lowered due to an acceleration of PSB formation.

B. The Effect of Microstructure on the Corrosion Fatigue Behavior of Austenitic-Ferritic Stainless Steels

The microstructural dependence of the corrosion fatigue behavior of austenitic-ferritic stainless steels is due to two independent effects, one mechanical and one electrochemical. The amount and distribution of each phase affects the fatigue behavior of these alloys in the absence of a corrosive environment, in a purely mechanical sense. Similarly, the nature and effect of the electrochemical dissolution taking place in a corrosive environment, either at a smooth surface or at a fatigue crack tip, is greatly affected by microstructure. Only when the two effects are combined can an accurate picture of the corrosion fatigue behavior

of this alloy system be formulated.

The mechanical effects of the microstructure on fatigue can be seen in the dependence of the tensile properties, fatigue life, and FCGR on ferrite volume fraction. The tensile data given in Figure 23 show that pure ferrite has a much higher yield strength but is much less ductile than pure austenite. As ferrite is added to an austenite matrix, strengthening accompanied by decreasing ductility occurs. When the microstructure contains at least 50% ferrite, the yield strength and ductility are representative of the matrix ferrite phase. Ferrite additions are able to strengthen an austenite matrix, for the stronger ferrite phase will not yield until long after the austenite matrix has. On the other hand, austenite additions to the ferrite matrix have little effect on yield strength or ductility, for the weaker austenite will yield with the ferrite, if not before.

The mechanical effects of microstructure on fatigue deformation are somewhat more complex. There is a tendency in duplex alloys for one phase to enhance crack initiation and retard crack propagation in fatigue, and vice versa. This tendency is due primarily to toughness differences between the two phases (99). A high toughness phase (in this case the austenite) can accommodate a large amount of plastic deformation before failing by a crack tip fracture mode, but undergoes extensive slip activity leading to more rapid crack initiation. The stronger, lower toughness phase (ferrite) undergoes slip less easily, but tends to fail by low energy fracture modes (pseudo-cleavage) once a crack is initiated.

Both austenite additions to a ferritic matrix and ferrite additions to an austenitic matrix improve total lifetime at a given stress level and crack growth resistance in air. Figures 31 and 38 show that maximum

fatigue resistance at low stress ratios occurs for Heat 226 (64% ferrite). This effect is mainly due to the ability of the duplex microstructure to disperse slip activity and distribute deformation more homogeneously, delaying crack initiation and forcing crack propagation to occur more uniformly. There is one exception to this trend. At $R = 0.6$, the crack propagation resistance is mostly dependent on yield strength, due to the low yield strength of the austenitic matrix alloys relative to the stress levels experienced. These effects will be illustrated fully in the following portions of the discussion dealing specifically with crack initiation and crack propagation behavior.

The electrochemical effects occurring for austenitic-ferritic stainless steels were studied by means of the abrading electrode tests and the accompanying polarization diagrams for the pure austenite and pure ferrite alloys. The polarization diagrams in Figure 45 showed that the kinetics of dissolution are much more rapid for austenite than for ferrite, both in the passive and freshly exposed conditions, probably due to a greater susceptibility of the austenite to pitting. When both phases are completely passivated, the rest potential of the austenite is slightly anodic to that of the ferrite. Therefore, in the absence of any freshly exposed metal (i.e. cracking), the austenite will undergo dissolution preferentially. The kinetics of this dissolution of the austenite phase are dependent not only on the fundamental anodic kinetics of the austenite as shown in the polarization diagrams, but also on the cathode-to-anode ratio, which in this case is the ferrite-to-austenite ratio. The larger the cathode/anode ratio is, the more rapid the anodic kinetics are.

This same ferrite/austenite ratio dependence is also important when

metal is freshly exposed at the crack tip. The results of the abrading electrode tests shown in Figures 42-44 are for a ferrite/austenite ratio of unity, and illustrate the electrochemical driving forces occurring at an opening crack tip. The most significant portion of these curves is the first few tenths of a second, because during fatigue at 10 cps, fresh metal is exposed every 0.1 second if crack growth is continuous. For the case in which both austenite and ferrite are freshly exposed at the crack tip, the austenite undergoes dissolution preferentially, the kinetics being fairly rapid and increasing with the ferrite/austenite ratio. If only one phase is freshly exposed at the crack tip, it will undergo dissolution, as it is highly anodic to the surrounding passive metal. However, because the dissolution kinetics of the austenite are much more rapid than that of the ferrite, there will be a significantly greater amount of dissolution at the crack tip when austenite alone is exposed than when ferrite alone is exposed, even though their repassivation rates are comparable. The consequences of these electrochemical effects on the actual corrosion fatigue behavior of this alloy system will be dealt with in the remainder of this discussion.

1. The Effect of Microstructure on Crack Initiation

The electrochemical studies have shown that when the austenite and ferrite phases are both in the passive state, which is surely the case prior to PSB formation and subsequent crack initiation, the austenite is anodic to the ferrite. Therefore, in any austenitic-ferritic microstructure, the acceleration of PSB formation due to surface dissolution can take place only in the austenite.

For Heat 225 (79% ferrite), there is no acceleration of crack initiation in the white water solution, despite the high ferrite/austenite ratio which increases the dissolution rate of the austenite. The reduction of lifetime in white water exhibited in the stress vs. cycles to failure tests are due solely to acceleration of FCGR as indicated in Figure 27. The passive dissolution of the austenite at the surface does not influence crack initiation because in this ferritic matrix alloy, the deformation in the form of PSB is concentrated in the ferrite phase, as shown in Figure 52. Since there is little deformation occurring in the austenite, dissolution does not affect crack initiation.

The same situation prevails for Heat 226 (64% ferrite) at the stress levels close to the fatigue limit. However, at a stress of 60 KSI (413.7 MPa), there is a significantly greater reduction of lifetime in white water than at lower stress levels. It is likely that this stress level is sufficiently high to produce significant cyclic deformation in the austenite as well as in the ferrite, hence accelerated PSB formation in the austenite due to dissolution becomes possible.

The acceleration of crack initiation by the environment is greatest for Heat 227 (34% ferrite). In this austenitic-matrix alloy, deformation is concentrated in the austenite, so acceleration of PSB formation due to surface dissolution of the austenite occurs. As there is little environmental acceleration of FCGR in this alloy, (Figure 29), the reductions in lifetime at alternating stress levels of 52 KSI (358.5 MPa) and 55 KSI (379.2 MPa) are totally due to accelerated crack initiation. At 60 KSI (413.7 MPa), PSB formation occurs so rapidly that the environmental effects on initiation become negligible.

matrix alloys, which all have approximately the same yield strength, an increase in austenite increases the roughness of the fracture surface, which translates into a decrease in FCGR. However, for the two austenitic-matrix alloys, the increase in roughness does not correspond to lower FCGR, because yielding ahead of the crack tip can occur at much lower ΔK values due to the lower yield strengths.

The effects of the white water environment are noticeable on ΔK_{th} and on FCGR at low ΔK . There are two independent effects responsible for environmental acceleration of FCGR and depression of ΔK_{th} . Electrochemical dissolution of austenite freshly exposed at the crack tip causes a significant decrease in crack growth resistance in the ferritic-matrix alloys containing austenite additions at $R = 0.05$. Apparent stress corrosion cracking effects accelerate FCGR in the alloys containing more than 30% austenite at $R = 0.6$.

The nature of electrochemical dissolution at an advancing crack tip in duplex stainless steels was studied by the abrading electrode tests. The situation where dissolution occurs most rapidly was shown to exist for an opening crack tip exposing both austenite and ferrite, or austenite in the vicinity of passive ferrite, with a high ferrite/austenite ratio. Acceleration of FCGR and decreases in ΔK_{th} occur due an increment of crack growth resulting from dissolution of the austenite and accompanying slight increases in stress intensity in the vicinity of the dissolution. This dissolution effect is responsible for increases in FCGR and decreases in ΔK_{th} for Heats 225 (79% ferrite) and 226 (64% ferrite) at $R = 0.05$. The effect of the environment is greater for Heat 225 because the ferrite/

Crack initiation in Heat 224 (100% ferrite) is accelerated by white water because there is no austenite present to prevent dissolution in the ferrite by forcing the ferrite to be the cathode. Thus local anodes and cathodes set up on the ferrite surface producing localized surface dissolution in the ferrite phase. This dissolution accelerates the PSB formation, causing a reduction in lifetime at all stress levels, as FCGR is not accelerated by the white water solution.

At a stress level of 52 KSI (358.5 MPa), the situation is similar for Heat 229 (6% ferrite), which should behave as a fully austenitic alloy. As there is no acceleration of FCGR by white water at $R = 0.05$, the reduction in lifetime must be due to accelerated crack initiation resulting from localized surface dissolution. However, at higher stress levels, the lifetimes are longer in white water than in air, indicating a retardation of crack initiation due to dissolution. This retardation occurs due to the combination of low yield strength and rapid anodic kinetics of the austenite. The alternating stress level is high enough above the yield strength that PSB formation is extremely rapid, resulting in very coarse PSB. The slip steps thus formed produce the exposure of fresh metal which can dissolve quite rapidly, delaying the development of the PSB into fatigue cracks by blunting the intrusions being formed. This action effectively reduces the stress concentration at the intrusions and thus retards crack initiation.

In comparing the overall corrosion fatigue crack initiation resistance of the five tie-line series alloys, the overriding factor is the high fatigue strength of Heat 226 (64% ferrite). In this alloy both microstructural phases accommodate the deformation by PSB formation,

which greatly inhibits slip localization that leads to crack initiation. Thus, despite being somewhat susceptible to an acceleration of crack initiation by the white water solution, this alloy exhibits the best corrosion fatigue crack initiation resistance of the tie-line series. Even though there is no environmental acceleration of crack initiation for Heat 225 (79% ferrite), its mechanical crack initiation resistance is not as great because all the deformation is accommodated by the ferrite, which comprises only 79% of the microstructure. The other three alloys suffer from environmental acceleration of crack initiation in addition to their inherently lower fatigue strength, causing their crack initiation resistance in white water to be even lower than for the ferritic-matrix duplex alloys.

The crack initiation resistance of the casting alloys with their much coarser microstructures has been previously studied (34). The findings were similar to this present study, showing that when the amount of austenite becomes sufficient to accommodate deformation through PSB formation, acceleration of crack initiation in white water occurred. For these casting alloys, accelerated initiation occurred for much lower volume fractions of austenite than for wrought alloys, because of the coarse distribution of the austenite which favors PSB localization. In addition, the presence of less austenite results in more rapid anodic kinetics for austenite dissolution, increasing the magnitude of environmental acceleration. The casting alloys therefore exhibit fatigue strengths in white water 30% lower than for wrought alloys within the same range of ferrite volume fraction.

The optimum microstructure for crack initiation resistance must

therefore be wrought to produce a fine distribution of the microstructural phases, which will disperse deformation. It should contain between 30% and 45% austenite in a ferrite matrix to produce maximum strengthening effects while simultaneously minimizing environmental acceleration of crack initiation. In this study, these requirements have been demonstrated by the superior corrosion fatigue crack initiation resistance of the alloy containing 64% ferrite.

2. The Effect of Microstructure on Crack Propagation

Just as for crack initiation, the mechanical effects of microstructural variations affect the FCGR in lab air. Figures 31 and 33 show that for the tie-line series alloys, FCGR in air are primarily dependent on the matrix phase for crack propagation resistance. At a stress ratio of $R = 0.05$, the ferritic-matrix alloys containing dispersed austenite, Heats 225 and 226, have the lowest FCGR in lab air. These two alloys have the highest yield strength in the tie-line series. The crack propagation resistance of the fully ferritic alloy ranks next, followed by the two austenitic-matrix alloys. The yield strengths of the austenitic-matrix alloys are too low to resist crack growth as well as the ferritic-matrix alloys do. The situation is similar at $R = 0.6$, where the three ferritic-matrix alloys have approximately the same FCGR in air, followed by the 36% ferrite and 6% ferrite alloys, respectively. Again, these FCGR rankings are due primarily to differences in yield strength.

At both low and high stress ratios in air, the fracture surfaces show primarily ductile fatigue features. The fracture surfaces become increasingly rough as the amount of austenite increases, indicating a greater amount of yielding ahead of the crack tip. For the ferritic-

austenite (cathode/anode) ratio is higher, producing more rapid dissolution of the austenite. These features are evident in Figures 35 and 36. These environmental effects disappear at high ΔK because the increment of crack growth due to dissolution is no longer significant as compared to the mechanical increment of crack advance. This dissolution effect is further substantiated by the SEM fractography. Figures 60 and 63 show actual dissolution of austenite on the fracture surfaces of Heats 225 and 226 at low ΔK . Although it is possible that this dissolution occurred following the passage of the crack tip, the absence of similar dissolution features on the fracture surfaces obtained at $R = 0.6$ suggest that this dissolution is a crack tip phenomenon occurring only at very low rates of mechanical crack growth. Electrochemical dissolution at the crack tip at $R = 0.05$ has little effect on Heat 224 (100% ferrite) because the anodic kinetics of the ferrite are too slow. Nor does dissolution affect the austenitic-matrix alloys, for the ferrite/austenite ratio is too low to produce enough dissolution.

At a stress ratio of $R = 0.6$, the situation is entirely different. Dissolution effects in Heats 225 and 226 are small because the mechanical increments of FCGR are much larger due to higher K_{max} at a given ΔK . A significant environmental acceleration of FCGR occurs only for the austenitic-matrix alloys and the 64% ferrite alloy, accompanied by decreases in ΔK_{th} . This acceleration may be due to SCC effects occurring at the fatigue crack tip, probably caused by hydrogen produced as the cathodic reaction product. At a stress ratio of $R = 0.6$, the maximum stress intensity at the crack tip, K_{max} , is quite high, being greater than twice ΔK . As SCC crack velocity is a function of K_{max} , and SCC

crack growth has been shown to occur for austenitic stainless steels within this $K_{\max}$ range (100), the increment of fatigue crack growth due to SCC is significant only when loading produces a low ΔK and a high $K_{\max}$ simultaneously. Although failure due to SCC does not generally occur for stainless steels at room temperature (84), SCC in austenitic stainless steels has been observed at temperatures as low as 40°C (101). Since some heating at an opening fatigue crack tip does occur, incremental crack growth due to SCC cannot be discounted on the basis of temperature. The existence of SCC effects under these conditions is supported by the fractography. Figures 66 and 70 show transgranular cleavage-like fracture features mixed with the ductile fatigue features at low ΔK , $R = 0.6$, for Heats 227 (66% austenite) and 229 (94% austenite). This cleavage-like fracture definitely seems to be the result of SCC in the austenite phase, as there is no other reasonable explanation for its appearance. SCC may also be responsible for the environmental reduction of ΔK_{th} in Heat 226 (36% austenite) at $R = 0.6$, as shown by the presence of cleavage-like features in the fractograph in Figure 64b. There is enough austenite present to cause crack growth to occur at a lower ΔK than in air due to SCC in the austenite, but since crack propagation occurs primarily in the ferrite, SCC has little effect on crack growth at ΔK levels much above ΔK_{th} . SCC effects are not significant in the other tie-line series alloys because ferrite is much more resistant to SCC (74,80, 82). SCC is not significant for the austenitic-matrix alloys at $R = 0.05$ because for a given ΔK , the maximum stress intensity at the crack tip, $K_{\max}$, is less than half the value that it is at $R = 0.6$. Because of the probable SCC effects in the austenite, the fully ferritic alloy has the

best crack growth resistance in white water at $R = 0.6$.

The environmental effects on FCGR at $R = 0.05$ observed for the wrought tie-line series alloys are contradicted by the FCGR behavior of the cast commercial alloys. Kelley, et. al. (2) showed no effect of white water solution on FCGR at 10 cps for VK-A171, VK-A271, and other cast duplex alloys. The wrought and cast alloys behave differently because of the scale of their microstructures. The austenite islands are much larger in the ferritic-matrix cast duplex alloys than in the wrought alloys. When fresh metal is exposed at an advancing crack tip, the ferrite/austenite ratio at the crack tip may be very different than the overall ratio because of the coarseness of the microstructure. Therefore, even though the overall cathode/anode ratio indicates that dissolution of the austenite will occur rapidly at the crack tip, the crack tip microstructure on a given cycle may be totally austenite or totally ferrite over a large distance across the crack tip, which serves to greatly reduce the galvanic cell action responsible for the accelerated FCGR in the wrought tie-line series alloys.

At $R = 0.6$, the cast alloys are susceptible to environmental acceleration of FCGR, as shown in Figure 24 for VK-A271. This acceleration is probably due to SCC effects in the austenite phase, which is large enough and accommodates enough deformation to play an important role in the FCGR resistance. Any SCC effects in the austenite may be much more important in the microstructurally coarse casting alloys, for in the wrought alloys they can be minimized by the supporting effect of the surrounding ferrite.

Although the cast alloys are resistant to environmental acceleration of FCGR at low stress ratio because of their coarse microstructure, other

problems detracting from their corrosion fatigue resistance are brought about by the coarse microstructure. The probable occurrence of SCC in the austenite at $R = 0.6$ was mentioned above. Notched-bar crack initiation is particularly sensitive to microstructure. The notched-bar S-N tests on VK-A171 and VK-A271, Figure 41, show that dissolution at or ahead of the notch does accelerate crack initiation at $R = 0.05$. This effect must be due to enhanced deformation in the austenite phase, just as occurs for smooth-bar crack initiation, as the presence of white water at a crack tip did not affect ΔK_{th} or low- ΔK FCGR in crack propagation studies. At $R = 0.6$, environmental effects disappear, but crack initiation is much more rapid than at $R = 0.05$ for a given stress range, due to the tendency for cleavage-like failure to occur in the ferrite phase. The wrought tie-line series alloys show a greater dependence of ΔK_{th} on R for the ferritic-matrix alloys than for the austenitic-matrix alloys because of this tendency. But this problem is much more serious in the cast alloys because the ferritic grain size is much larger. When a ferrite grain has the proper crystallographic orientation, cleavage-like fracture can occur at high stress ratios accompanied by ductile tearing in the austenite, as shown in Figure 73 for alloy VK-A271. If a properly oriented ferrite grain lies at the notch tip, crack initiation at $R = 0.6$ will be quite rapid, as will subsequent crack propagation until the grain boundary is reached. The same cleavage-like fracture effect can accelerate FCGR locally, as shown by the large amount of data scatter in the FCGR curves for VK-A271 at $R = 0.6$, Figure 24. Even at $R = 0.05$, crack growth in the ferrite phase is more rapid than in the austenite for the cast alloys, as shown in Figure 72.

The effect of microstructural orientation is much less significant in the wrought alloys, due to their finer microstructures. Tests investigating the dependence of FCGR on orientation for wrought Uranus 50 showed crack growth in the longitudinal direction was slightly more rapid than in the transverse direction. This orientation dependence occurs because the microstructure appears more homogeneous in the transverse direction, and a crack growing in the transverse direction will encounter more phase boundaries perpendicular to its path. Both of these features will tend to retard crack propagation. This same orientation dependence was observed by Liljas and Fridberg (4) for wrought 3RE60. Uranus 50 exhibited little environmental dependence of FCGR at $R = 0.05$ because it contains about 65% austenite, resulting in a small cathode/anode ratio.

3. The Best Microstructure for Corrosion Fatigue Resistance

The studies on the wrought tie-line series alloys showed that the alloy exhibiting the best performance in white water solution at low stress ratio, both in cycles to failure and FCGR tests, contained 64% ferrite and 36% austenite. Compared to a cast alloy with similar volume fractions of each phase (34), the number of cycles to failure at a given stress level is much greater for the wrought alloy. The wrought alloy is superior despite the fact that the FCGR at $R = 0.05$ for the cast alloy are not affected by the presence of the white water solution. The crack initiation resistance of the wrought alloy is thus much greater than the cast alloy. When high stress ratios are considered, the wrought alloy is again preferred because it is not as susceptible to cleavage-like fracture in the ferrite phase, or to SCC in austenite within a ferritic matrix. However, higher ferrite fractions are desirable in the wrought alloys to

eliminate SCC effects.

There has been concern that even though the wrought alloys perform better because their microstructures can be easily controlled, the formation of harmful precipitates during welding will detract from corrosion fatigue resistance. These fears appear to be unfounded. Liljas (89) has shown that sigma phase formation causes only a slight decrease in corrosion fatigue resistance in wrought 3RE60, and that this decrease is due to mechanical and not electrochemical effects. Tedmon and Vermilyea (81) have concluded that sensitization during welding should not affect intergranular corrosion resistance (which obviously can affect corrosion fatigue resistance) because the phase boundaries will migrate away from the sensitized region.

The key point in selecting an austenitic-ferritic stainless steel microstructure for corrosion fatigue resistance is a consideration of the application. For certain applications where crack initiation resistance is not important, cast alloys may outperform wrought alloys because their FCGR are less sensitive to a corrosive environment. If high residual stresses are present after fabrication or if the loading sequence includes high stress ratios, wrought alloys with higher ferrite contents become more desirable. Fully ferritic alloys are capable of outperforming duplex alloys under such conditions, where the major detriment to corrosion fatigue resistance is apparent SCC in the austenite. However, in most common applications where no incipient cracks are present and the stress ratio is low, wrought austenitic-ferritic alloys containing 50-70% ferrite will provide the best corrosion fatigue resistance, for they offer the best available combination of crack initiation and crack propagation

resistance.

VI. CONCLUSIONS

1. Plastic deformation of metals in the absence of cracking is accelerated by surface dissolution, due to changes in dislocation activity caused either by the dissolution of surface dislocation tangles or by possible changes in the thickness of surface oxide layers.

2. Fatigue crack initiation occurs more rapidly under the influence of electrochemical dissolution because the formation of persistent slip bands which precede crack initiation is accelerated.

3. The corrosion fatigue resistance in reverse bending for wrought austenitic-ferritic stainless steels is greatest for alloys containing around 60% ferrite and 40% austenite, due to the ability of this microstructure to disperse slip activity and delay crack initiation. Also, for these wrought ferritic-matrix alloys, crack initiation occurs in the ferrite and is therefore unaffected by dissolution, which must occur in the austenite.

4. The corrosion fatigue crack propagation resistance at $R = 0.05$ is greatest for alloys containing around 60% ferrite and 40% austenite because the mechanical fatigue crack propagation resistance is highest, and the effect of electrochemical dissolution decreases as the austenite fraction increases.

5. Acceleration of FCGR in white water solution at $R = 0.05$ occurs only for ferritic-matrix alloys containing austenite islands. This acceleration appears to be due to the electrochemical dissolution of austenite at the crack tip, which increases with increasing cathode/anode (ferrite/austenite) ratio.

6. Acceleration of FCGR in white water solution at $R = 0.6$ occurs

only for alloys containing more than 30% austenite. This acceleration appears to be due to the occurrence of stress corrosion cracking in the austenite. Consequently, the corrosion fatigue crack propagation resistance at $R = 0.6$ is greatest for the fully ferritic alloy.

7. A corrosive environment does not accelerate FCGR at $R = 0.05$ in cast alloys, because the coarseness of the cast microstructure reduces the galvanic action at the crack tip. SCC effects in the austenite may be responsible for accelerated FCGR at $R = 0.6$, and can be more detrimental than for wrought alloys due to the increased size of the austenite islands.

8. The selection of the proper austenitic-ferritic microstructure must be made with a knowledge of the loading and environmental variables involved in the particular application. The relative corrosion fatigue resistance of these alloys is sensitive both to stress ratio and to the relative hostility of the environment. Austenitic-ferritic stainless steels in general exhibit good corrosion fatigue resistance, and offer the opportunity for that resistance to be greatly increased for specific applications through microstructural manipulation.

VII. SUGGESTIONS FOR FURTHER WORK

1. Study the interrelationships of PSB spacing, oxide film thickness, and anodic current density in corrosion fatigue. This study would provide additional information concerning the mechanisms of corrosion fatigue crack initiation.
2. Study the effects of texture on the fatigue and corrosion fatigue behavior of austenitic-ferritic stainless steels. Certain textures may increase initiation and FCGR resistance, either by strengthening the alloy further or by minimizing SCC effects.
3. Compare the corrosion fatigue resistance of commercially available molybdenum-containing ferritic specialty stainless steels to that of austenitic-ferritic stainless steels.
4. Investigate the possibility of a strain-induced martensitic transformation occurring at the crack tip within the austenite phase in duplex stainless steels.
5. Develop a technique to monitor actual electrochemical dissolution transients at a corrosion fatigue crack tip in duplex stainless steels.
6. Study the corrosion behavior, both in the absence and presence of strain, by the scanning reference electrode technique developed by Vyas, Isaacs, and Weeks (102).

VII. REFERENCES

1. J. W. Flowers, F. H. Beck, and M. G. Fontana, Corrosion, 19 (1963), 1864.
2. G. E. Kelley, J. Vestola, V. Sailas, and R. M. Pelloux, TAPPI, 58 (1975), 80.
3. R. M. Vadas and R. Thompson, Pulp and Paper Magazine of Canada, 72 (1971), T336.
4. M. Liljas and J. Fridberg, "Avesta 3RE60 - A New Stainless Steel for Suction Rolls," presented at International Seminar on Pulp and Paper Industry Corrosion Problems, Chicago, 1974.
5. O. F. Devereux, A. J. McEvily, and R. W. Staehle, Eds., Corrosion Fatigue: Chemistry, Mechanics, and Microstructure, NACE, Houston, 1972.
6. R. M. Pelloux, R. E. Stoltz, and J. A. Moskovitz, Mat. Sci. Eng., 25 (1976), 193.
7. C. Laird and D. J. Duquette, in Corrosion Fatigue: Chemistry, Mechanics, and Microstructure, NACE, Houston, 1972, p. 88.
8. R. P. Wei and A. J. Baker, Philos. Mag., 11 (1965), 1087.
9. R. P. Wei and A. J. Baker, Philos. Mag., 12 (1965), 1005.
10. P. Lukas and M. Klesnil, in Corrosion Fatigue: Chemistry, Mechanics, and Microstructure, NACE, Houston, 1972, p. 118.
11. J. C. Grosskreutz and H. Mughrabi, in A. S. Argon (ed.), Constitutive Equations in Plasticity, M.I.T. Press, Cambridge, Mass., 1975, p. 251.
12. D. Kuhlmann-Wilsdorf and C. Laird, Mat. Sci. Eng., 27 (1977), 137.
13. S. J. Basinski, Z. S. Basinski, and A. Howie, Philos. Mag., 31 (1975), 899.
14. I. R. Kramer and A. Kumar, in Corrosion Fatigue: Chemistry, Mechanics, and Microstructure, NACE, Houston, 1972, p. 146.
15. C. Laird, Mat. Sci. Eng., 22 (1976), 231.
16. C. Laird, in A. W. Thompson (ed.), Work Hardening in Tension and Fatigue, AIME, New York, 1977, p. 150.

17. R. M. Latanision and J. T. Fourie (eds.), Surface Effects in Crystal Plasticity, Noordhoff, Leyden, The Netherlands, 1977.
18. V. I. Likhtman, E. D. Shchukin, and P. A. Rebinder, Physico-Chemical Mechanics of Metals, Israel Program for Scientific Translations, Jerusalem, 1964.
19. J. C. Grosskreutz, in Corrosion Fatigue: Chemistry, Mechanics, and Microstructure, NACE, Houston, 1972, p. 201.
20. L. C. deJonghe and I. G. Greenfield, Acta Met., 17 (1969), 1411.
21. W. R. Patterson and I. G. Greenfield, Acta Met., 19 (1971), 123.
22. I. G. Greenfield, in Corrosion Fatigue: Chemistry, Mechanics, and Microstructure, NACE, Houston, 1972, p. 133.
23. I. G. Greenfield and A. Purohit, in Surface Effects in Crystal Plasticity, Noordhoff, Leyden, The Netherlands, 1977, p. 609.
24. E. Y. Chen and E. A. Starke, Jr., Mat. Sci. Eng., 24 (1976), 209.
25. T. Takasugi and O. Izumi, Acta Met., 24 (1976), 1107.
26. D. H. Bradhurst and J. S. L. Leach, Trans. Brit. Ceramic Soc., 62 (1963), 793.
27. J. S. L. Leach and P. Neufeld, Proc. Brit. Ceramic Soc., 6 (1966), 49.
28. J. C. Grosskreutz, Surface Science, 8 (1967), 173.
29. J. C. Grosskreutz, J. Electrochem. Soc., 117 (1970), 940.
30. R. Gibala and V. K. Sethi, in Surface Effects in Crystal Plasticity, Noordhoff, Leyden, The Netherlands, 1977, p. 599.
31. D. Howard and T. Pyle, Brit. Corr. J., 3 (1968), 302.
32. T. Pyle, V. Rollins, and D. Howard, in Corrosion Fatigue: Chemistry, Mechanics, and Microstructure, NACE, Houston, 1972, p. 312.
33. T. Pyle, V. Rollins, and D. Howard, J. Electrochem. Soc., 122 (1975), 1445.
34. J. A. Moskovitz, S. M. Thesis, M.I.T., Cambridge, Mass., 1975.
35. D. J. Duquette and H. H. Uhlig, ASM Trans. Q., 62 (1969), 839.
36. H. H. Lee and H. H. Uhlig, Met. Trans., 3 (1972), 2949.

37. R. W. Revie and H. H. Uhlig, Acta Met., 22 (1974), 619.
38. A. I. Asphahani, Ph.D. Thesis, M.I.T., Cambridge, Mass., 1975.
39. P. L. Andresen and D. J. Duquette, submitted for publication, 1975.
40. H. Hahn and D. J. Duquette, submitted for publication, 1975.
41. D. J. Duquette, H. Hahn, and P. Andresen, in Surface Effects in Crystal Plasticity, Noordhoff, Leyden, The Netherlands, 1977, p. 469.
42. R. M. Latanision and A. R. C. Westwood, in Advances in Corrosion Science and Technology, Vol. 1, Plenum Press, New York, 1970, p. 51.
43. R. M. Latanision, H. Oppenhausser, Jr., and A. R. C. Westwood, in Proceedings of the Fifth International Congress on Metallic Corrosion, NACE, Houston, 1974, p. 111.
44. R. M. Latanision and R. W. Staehle, Acta Met., 17 (1969), 307.
45. H. H. Uhlig, J. Electrochem Soc., 123 (1976), 1699.
46. R. L. Prowse and M. L. Wayman, Corrosion, 30 (1974), 280.
47. R. W. Staehle, Mat. Sci. Eng., 25 (1976), 207.
48. J. M. Barsom and R. C. McNicol, in Fracture Toughness and Slow-Stable Cracking, ASTM STP 559, ASTM, Philadelphia, 1974, p. 183.
49. M. Klesnil and P. Lukas, Mat. Sci. Eng., 9 (1972), 238.
50. J. Masounave and J. P. Babilon, Scripta Met., 9 (1975), 723.
51. R. O. Ritchie, submitted to Journal of Eng. Mat. and Tech., Trans ASME, Series H, 1976. Available as Lawrence Berkeley Laboratory preprint no. LBL-5496.
52. D. B. Dawson and R. M. Pelloux, Met. Trans., 5 (1974), 723.
53. R. P. Wei and J. D. Landes, Mat. Res. Stand., 9 (1969), 25.
54. W. W. Gerberich, J. P. Birat, and V. F. Zackay, in Corrosion Fatigue: Chemistry, Mechanics and Microstructure, NACE, Houston, 1972, p. 396.
55. M. O. Speidel, M. J. Blackburn, T. R. Beck, and J. A. Feeney, in Corrosion Fatigue: Chemistry, Mechanics, and Microstructure, NACE, Houston, 1972, p. 324.

56. T. Misawa, N. Ringshall, and J. F. Knott, Corrosion Science, 16 (1976), 805.
57. K. Endo and K. Komai, in Corrosion Fatigue: Chemistry, Mechanics, and Microstructure, NACE, Houston, 1972, p. 437.
58. R. J. Selines and R. M. Pelloux, Met. Trans., 3 (1972), 2525.
59. J. M. Barsom, in Corrosion Fatigue: Chemistry, Mechanics, and Microstructure, NACE, Houston, 1972, p. 424.
60. F. P. Ford and T. P. Hoar, submitted to J. Electrochem. Soc., 1975.
61. P. Engseth and J. C. Scully, Corrosion Science, 15 (1975), 505.
62. N. D. Tomashov and G. P. Chernova, Passivity and Protection of Metals Against Corrosion, Plenum Press, New York, 1967.
63. M. Gell and D. J. Duquette, in Corrosion Fatigue: Chemistry, Mechanics, and Microstructure, NACE, Houston, 1972, p. 366.
64. J. D. Fransden, W. L. Morris, and H. L. Marcus, North American Rockwell Science Center Preprint, SC-PP-73-84, Oct. 1973.
65. R. M. Latanision, in Surface Effects in Crystal Plasticity, Noordhoff, Leyden, The Netherlands, 1977, p. 3.
66. W. R. Tyson and L. C. R. Alfred, in Corrosion Fatigue: Chemistry, Mechanics, and Microstructure, NACE, Houston, 1972, p. 281.
67. R. E. Stoltz and R. M. Pelloux, Met. Trans., 3 (1972), 2433.
68. R. E. Stoltz and R. M. Pelloux, Corrosion, 29 (1973), 13.
69. ASM Metals Handbook, Vol. 8, American Society for Metals, Metals Park, Ohio, 1973, p. 424.
70. L. Pryce and K. W. Andrews, J. Iron and Steel Inst., 195 (1960), 415.
71. A. L. Schaeffler, Metal Progress, 56 (1949), 680.
72. P. Guiraldenq, Mem. Sci. Rev. Met., 64 (1967), 907.
73. P. Jolly, Bulletin du Cercle d'Etudes des Metaux, 12 (1973), 317.
74. G. M. Gordon, in Proceedings of International Conference on SCC and Hydrogen Embrittlement of Iron-Base Alloys, Unieux, Firminy, France, 1973, in press. Also published as G. E. Technical Information Series, No. 73NED105, General Electric Co., Pleasanton, Calif., 1973.

75. H. W. Hayden and S. Floreen, Met. Trans., 1 (1970), 1955.
76. P. Jolly and J. Hochmann, Mem. Sci. Rev. Met., 70 (1973), 117.
77. F. Lecroisey and A. Pineau, Met. Trans., 3 (1972), 387.
78. K. Wakasa and T. Nakamura, Scripta Met., 10 (1976), 129.
79. F. Nair and M. Semchyshen, Corrosion, 19 (1963), 2104.
80. R. L. Cowan and G. M. Gordon, G. E. Technical Information Series, No. 73NED106, General Electric Co., Pleasanton, Cal., 1973.
81. C. S. Tedmon, Jr., and D. A. Vermilyea, Met. Trans., 1 (1970), 2043.
82. W. L. Clarke, J. C. Danko, and G. M. Gordon, G. E. Technical Information Series, No. 74NED57, General Electric Co., Pleasanton, Cal., 1974.
83. S. Shimodaira, M. Takano, K. Takizawa, and H. Kamide, Proceedings of International Conference on SCC and Hydrogen Embrittlement of Iron-Base Alloys, Unieux, Firminy, France, 1973, in press.
84. R. M. Latanision and R. W. Staehle, in Fundamental Aspects of Stress Corrosion Cracking, NACE, Houston, 1969, p. 214.
85. N. A. Nielsen, in Fundamentals Aspects of Stress Corrosion Cracking, NACE, Houston, 1969, p. 308.
86. F. H. Beck, J. Juppenplatz, and P. F. Wieser, in H. L. Craig, Jr. (ed.), Stress Corrosion - New Approaches, ASTM STP 610, American Society for Testing and Materials, Philadelphia, 1976.
87. H. W. Hayden and S. Floreen, Met. Trans., 4 (1973), 561.
88. C. Lemaignan, S. M. Thesis, M.I.T., Cambridge, Mass., 1973.
89. M. Liljas, "Influence of Precipitates on Corrosion Fatigue Properties of a Duplex Stainless Steel," internal document, Avesta Jernverks AB, Avesta, Sweden, 1975.
90. ASTM Standard E8-69, American Society for Testing and Materials, Philadelphia, 1971.
91. H. Tada, P. Paris, and G. Irwin, The Stress Analysis of Cracks Handbook, Del Research Corp., Hellertown, Pa., 1974.
92. F. I. Baratta, J. I. Bluhm, G. W. Driscoll, and W. T. Matthews, Int. J. Fracture Mech., 7 (1971), 203.

93. H. H. Uhlig, Corrosion and Corrosion Control, Wiley, New York, 1971.
94. M. G. Fontana and N. D. Greene, Corrosion Engineering, McGraw-Hill, New York, 1967.
95. N. D. Greene, Experimental Electrode Kinetics, Rensselaer Polytechnic Institute, Troy, New York, 1965.
96. N. D. Tomashov, Theory of Corrosion and Protection of Metals, Macmillan, New York, 1966.
97. M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, NACE, Houston, 1974.
98. L. Antropov, Theoretical Electrochemistry, Mir Publishers, Moscow, 1972.
99. R. M. Pelloux and R. E. Stoltz, in Proceedings, Fourth International Conference on the Strength of Metals and Alloys, Nancy, France, 1976, p. 1023.
100. H. Lefakis and W. Rostoker, Corrosion, 33 (1977), p. 178.
101. D. Warren, Proceedings of the Fifteenth Annual Industrial Waste Conference, Purdue University, 1960.
102. B. Vyas, H. S. Isaacs, and J. R. Weeks, Brookhaven National Laboratory Report BNL-NUREG-50596, Brookhaven National Laboratory, Upton, N. Y., 1976.

APPENDIX: PROCEDURE FOR NORMALIZATION OF CREEP DATA

In order to account for the reduction in cross-sectional area of the wire specimens due to dissolution during the creep tests, the following procedure was used to normalize the creep rates.

1. The total number of coulombs passed during the entire creep test ($\Sigma \text{current} \times \text{time}$) was calculated.
2. The reduction in specimen radius at the end of the test was divided by the number of coulombs to give a value of reduction in radius per coulomb.
3. The specimen radius at the end of each creep increment for a given applied current density was calculated based on the number of coulombs passed.
4. The actual specimen stress was calculated for each creep increment based on the reduced cross-sectional area.
5. The measured creep rate for each creep increment was multiplied by the ratio of nominal stress/actual stress to yield a value of normalized creep rate. This normalization procedure is valid, as Uhlig (45) has shown a linear relationship between creep rate and applied stress for this type of test.

BIOGRAPHICAL NOTE

The author was born and raised in Lexington, Ky., where he graduated from Tates Creek High School in 1969. He entered the Georgia Institute of Technology in 1969, receiving the B.S. degree with highest honors in 1973. He entered M.I.T. in 1973, receiving the S.M. degree in Metallurgy in 1975. Following receipt of his Ph.D. degree, the author will assume a faculty position in the Department of Mechanical Engineering of the University of California, Davis.