PITTING AND STRESS CORROSION CRACKING ~

IN ALLOY 200

٣

By

RAJU S. KALIDINDI

Bachelor of Engineering Bangalore University Bangalore, India 1984

Master of Technology Kakatiya University Warangal, India 1987

Submitted to the Faculty of the Graduate College of the Oklahoma State University in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE December, 1991 . .

The second secon

Ciaedl 1971 44134

Oklahoma State Univ. Library

PITTING AND STRESS CORROSION CRACKING IN ALLOY 200

Thesis Approved:

Thesis Adviser

Dean of the Graduate College

ACKNOWLEDGEMENTS

I would like to express my sincere thanks to Dr. C. E. Price, my major advisor, for his continuous guidance and constant encouragement throughout my graduate studies at Oklahoma State University. His scholarly instructions and invaluable suggestions are highly appreciated. I am very grateful to Dr. Y. C. Shiau and Dr. J. K. Good for graciously serving on my committee.

The School of Mechanical and Aerospace Engineering at Oklahoma State University is gratefully acknowledged for providing me a teaching assistantship during my graduate study.

My profound gratitude to my parents and other family members and friends for their encouragement and support.

Finally, my special thanks to my wife, Praveena, and son, Vamsi for their love and understanding to successfully complete my graduate studies.

TABLE OF CONTENTS

Chapter		Page
I.	INTRODUCTION	. 1
II.	A SELECTED LITERATURE REVIEW	. 4
	Alloy 200	. 4 . 8 . 11 . 13
III.	PROPOSED INVESTIGATIONS	20
IV.	EXPERIMENTAL PROCEDURE>	22
	Immersion Tests	22 24
V.	EXPERIMENTAL RESULTS	28
	Immersion Test Results . <td>28 . 55</td>	28 . 55
VI.	DISCUSSION AND ANALYSIS	. 76
VII.	CONCLUSIONS	85
SELECT	TED BIBLIOGRAPHY	. 87
APPENI	DIX - THEORIES OF PITTING CORROSION	. 91

LIST OF TABLES

Table Page
I. Chemical Composition of Alloy 200
II. Room Temperature Mechanical Properties of Alloy 200 5
III. Immersion Tests in Ferric chloride solutions
IV. Immersion Tests in Cupric chloride solutions
V. Immersion Tests in Ammonium persulfate solutions
VI. Follow up Immersion Tests
VII. Observations AFTER Chemical polishing
VIII. Immersion Tests on Chemically polished samples
IX. Observations in SCC Tests by SST method

LIST OF FIGURES

Figur	re	Pa	ige
1.	Corrosion of Alloy 200 in Hydrochloric acid solution at 30 C		7
2.	Isocorrosion chart for Alloy 200 in Sodium hydroxide	•	7
3.	Schematic sketch of three possible initiation processes for Pitting: (a) through incorporation of Anions into the Oxide, (b) through island Adsorption of on the Passive oxide, and (c) through tearing of the Passive oxide		9
4.	Schematic Representation of Film-Rupture Mechanism for Stress Corrosion Cracking		15
5.	(a) through (f). Schematic Representation of Film-Rupture Mechanism for Stress Corrosion Cracking of Brass (g) Resulting Fracture surface	•	16
6.	Geometry of Tensile Specimen	•	25
7.	Schematic of Specimen Arrangement on MTS machine		27
8.	The Corrosion attack of Alloy 200 in 0.04M Ferric chloride solution for 48 hours shows General attack and different sizes of pits	•	31
9.	The Corrosion attack of Alloy 200 in 0.04M Ferric chloride solution for 24 hours shows some General attack and Pitting		31
10.	The Pitting attack of Alloy 200 in 0.004M Ferric chloride solution for 12 hours shows few small size pits	•	32
11.	The Pitting attack of Alloy 200 in 0.002M Ferric chloride solution for 12 hours shows some small size pits	•	32
12.	Effect of Concentration on Pitting Behavior in Ferric chloride at 24 hours duration		33
13.	Effect of Time of immersion in 0.004M Ferric chloride		35
14.	The Pitting attack of Alloy 200 in 0.293M Cupric chloride solution for 24 hours many big and small size deep pits on top surface		39
15.	The bottom surface of the above sample showing Pitting and severe Crevice attack		39

Figure

16.	The Pitting attack of Alloy 200 in 0.293M Cupric chloride solution for 12 hours shows many pits and some Crevice attack on bottom surface 40
17.	The Pitting attack of Alloy 200 in 0.176M Cupric chloride solution for 24 hours shows many small size pits and slight crevice attack
18.	The Pitting attack of Alloy 200 in 0.176M Cupric chloride solution for 12 hours shows few small size pits and slight Crevice attack on bottom surface 41
19.	The Pitting attack of Alloy 200 in 0.0586M Cupric chloride solution for 12 hours shows few big and small size pits on top surface
20.	Effect of Time of immersion in 0.0586M Cupric chloride
21.	Effect of Concentration on Pitting Behavior in Cupric chloride at 24 hours duration
22.	The Pitting attack of Alloy 200 in 0.029M Cupric chloride solution for 24 hours shows small size pits on top surface
23.	The Pitting attack of Alloy 200 in 0.029M Cupric chloride solution for 72 hours shows few small size deep pits on top surface
24.	The Pitting attack of Alloy 200 in 0.006M Cupric chloride solution for 12 hours shows few deep pits on top surface
25.	The Corrosion attack of Alloy 200 in 0.029M Cupric chloride and 10% Hydro-chloric acid shows severe General corrosion and few pits
26.	The Corrosion attack of Alloy 200 in 0.219M Ammonium persulfate solution for 24 hours shows General corrosion and Crevice attack on bottom surface 49
27.	The Corrosion attack of Alloy 200 in 0.134M Ammonium persulfate solution for 24 hours shows General corrosion and slight Crevice attack 49
28.	The Corrosion attack of Alloy 200 in 0.044M Ammonium persulfate solution for 24 hours shows Pitting leading to General corrosion and slight crevice attack
29.	The Pitting attack of Alloy 200 in 0.022M Ammonium persulfate solution for 48 hours shows small size deep pits on top surface
30.	The Pitting attack of Alloy 200 in Aerated 80% Ammonium hydroxide for 48 hours shows some small size pits on top
31.	The Pitting attack of Alloy 200 in 26% Hydrofluoric acid for 48 hours shows small deep pits on top
32.	The Chemically polished surface of Alloy 200 at 95 C for 60 seconds shows many big and small size pits

Figure

33.	The Corrosion attack of Chemically polished Alloy 200 in 0.04M Ferric chloride solution for 24 hours shows Pitting attack leading to General corrosion 57
34.	The Pitting attack of Chemically polished Alloy 200 in 0.03M Cupric chloride solution for 24 hours shows many small size pits
35.	The Pitting attack of Chemically polished Alloy 200 in 0.044M Ammonium persulfate solution for 24 hours shows Pitting leading to General attack 58
36.	The Pitting attack of Chemically polished Alloy 200 in 0.02M Ferric chloride solution for 48 hours shows many small size pits
37.	The Pitting attack of Chemically polished Alloy 200 in 0.006M Cupric chloride solution for 48 hours shows few small size pits
38.	The Pitting attack of Chemically polished Alloy 200 in 0.022M Ammonium persulfate solution for 48 hours shows pitting leading to General attack 60
39.	The side view of the fracture zone in 0.4M Ferric chloride solution. Extensive gaping cracks are seen in the vicinity of the fracture
40.	The test details of the Figure 39 showing severe General attack and extensive gaping cracks
41.	The test details of the Figure 40 at higher magnification
42.	The test details of Figure 39. The surface away from the fracture vicinity, showing General attack and elongated pits in the form of longitudinal cavities. The cracking is minimal
43.	The test details of the Figure 42 at higher magnification
44.	The side view of the fracture zone in 0.12M Ferric chloride solution. The transverse cracking with gaping is observed in the vicinity of fracture. The cracking is less extensive compared to Figure 39
45.	The test details of figure 44 showing Pitting attack leading to General corrosion and gaping cracks
46.	The test details of the Figure 45 at higher magnification
47.	The test details of the Figure 44. The surface away from the fracture vicinityshowing some corrosion and longitudinal cracks. The corrosion attack is less severe than in Figure 42
48.	The test details of the Figure 47 at higher magnification
49.	The side view of the fracture zone in 0.02M Ferric chloride solution. The surface shows many small pits and cracks. The gaping is less extensive than in Figures 39 and 44

Figur	e	Page
50.	The test details of figure 49 showing less corrosion attack and cracking compared to figures 40 and 45	. 70
51.	The test details of Figure 50 at higher magnification	. 71
52.	The test details of Figure 49. The surface away from the fracture vicinity showing some elongated pits. The corrosion attack is less severe than in Figures 42 and 47	. 71
53.	The side view of the fracture zone in 0.03M Cupric chloride solution. The cracking is minimal compared to tests in Ferric chloride solutions. Extensive deformation and many pits are visible	. 73
54.	The test details of figure 53 showing minimal cracking and corrosion attack	. 73
55.	The side view of the fracture zone in 0.04M Ammonium persulfate solution. The cracking is minimal compared to tests in Ferric chloride solutions. Numerous pits are visible on the fracture surface	. 74
56.	The test details of Figure 55 showing little cracking and corrosion attack compared to Figure 54	. 74
57.	The test details of the Figure 56 at higher magnification	. 75
58.	Various Configurations of Pits	. 80

.

CHAPTER I

INTRODUCTION

Corrosion can be defined as the reaction of a metallic material with its environment. The products of this reaction may be solid, liquid or gaseous. Both the physical and chemical natures of the products are important since they frequently influence the subsequent rate of reaction. The study of Corrosion needs neither justification nor explanation. Every metal producer and user is forced to undertake it. In announcing the signing of the NACE-NBS agreement, the United states department of commerce stated, "Corrosion will cost the United states an estimated \$126 billion in 1982" [1]. With the increasing use of metallic materials these figures would update to approximately \$200 billion in 1992. About 20% of these costs could be saved by the available sound engineering practice. It is estimated that a developed country spends almost four percent of its GNP on metallic corrosion and its protection [2]. The corrosion of metals, therefore represents a terrible waste of both natural resources and money.

Nickel and nickel-base alloys have an important role in modern industry. This popularity is due to their ability to withstand a wide variety of operating conditions involving corrosive environments, high temperatures, and high stresses [3]. These alloys are used in a variety of applications including oil, food, dairy, power, textile and chemical industries. Pure nickel is ductile and tough because it possesses a face-centered cubic crystal structure. Nickel can accommodate large amounts of alloying elements, including chromium, molybdenum, and tungsten. It is possible due to its atomic size and nearly complete 3d electron shell. Nickel and some of its alloying elements form intermetallic phases, which enables the formulation of high strength alloys for both low temperature and

high temperature service. Some of the useful categories of nickel-base alloys are commercially pure nickel, nickel-copper, nickel-chromium, nickel-chromium-iron, and nickel-chromium-molybdenum. The nickel-base super alloys such as MP35N, Alloy C276, the 600, and 800 series alloys are more widely used than stainless steels in extremely subversive environments.

Nickel-base alloys are frequently used because of their improved resistance to environmental embrittlement over steels and stainless steels. However, nickel-base alloys can exhibit environmental embrittlement under the combined action of tensile stresses and specific environmental conditions [3]. Liquid metal embrittlement [LME], hydrogen embrittlement [HE], and stress corrosion cracking [SCC] are often considered together, compared and contrasted under the more general heading of environmentally assisted cracking [EAC]. SCC is often associated with intergranular cracking or pitting attack. These two forms of localized corrosion can produce stress concentrations which act as crack initiation sites for stress cracking to occur.

The assignment for this thesis was concise, "Endeavor to obtain SCC in the nickel Alloy 200 at room temperature and explore any correlation with pitting behavior". Alloy 200 (NO2200) is a commercially pure metal about 99.9 wt% nickel.

The background to this charge is as follows. Price and Good have demonstrated that seemingly any nickel base alloy can be embrittled by liquid mercury and by hydrogen at room temperature [4, 5]. If failure occurs at low strains, the cracking is intergranular, with a transition to transgranular at intermediate strains, 0.2-0.5. More recently, these studies on nickel- base alloys have been extended to SCC. SCC has been recognized to occur in some nickel-base alloys at elevated temperatures but little has been reported on the behavior at room temperature. SCC has been reported in Alloys 200, 400, and 600 in polythionic acids at room temperature [3]. In particular SCC has become a problem in nuclear power plants where traces of chlorides have lead to cracking in Alloy 600 in the temperature range of 200-300 C [6, 7].

The alloys most extensively studied at Oklahoma State University have been 200, 400, 600, and 800 [9, 10, 11, 13, 14, 15]. Accordingly, when the SCC program began, the thrust was to concentrate on the same alloys beginning with Alloy 400, because this is the nickel base alloy most effectively embrittled by hydrogen and by mercury [4, 5, 8, 9, 10]. Everhart [11, 12] demonstrated SCC in Alloy 400 at room temperature in the solutions of ferric chloride, cupric chloride, and ammonium persulfate. In a follow up study, Lu [13] demonstrated the threshold conditions and explored the pitting behavior. Hussen [14] has since demonstrated pitting and SCC in ferric chloride solutions in alloy 600. Zaheer [15] obtained pitting but not SCC in ferric chloride with alloy 800. However, Zaheer did point out the effect of a sensitization heat treatment on the pitting behavior and LME by mercury, an aspect somewhat ignored in the previous studies at this school [11, 13]. Furthermore, Zaheer [15] noted that some embrittlement in ferric chloride did occur in corrosion fatigue testing.

Alloys 400, 600, and 800 were studied before alloy 200 because SCC is relatively difficult to get in pure materials [16, 17]. In this present study, pitting tests are done in ferric chloride, cupric chloride, ammonium persulfate, hydrofluoric acid, and in some alkalies. These are the aggressive environments that cause pitting in most of the nickelbase alloys. The test parameters are solution concentration, surface condition and time of exposure. An attempt has been made to study whether there is any difference in pitting behavior of specimens polished by chemical and mechanical methods. Pitting tests are followed by SCC tests on indented specimens, and on waisted tensile samples by slow strain rate tests [SST].

CHAPTER II

A SELECTED LITERATURE REVIEW

Alloy 200

Alloy 200 has excellent corrosion resistance to many corrosive environments [1]. The chemical composition of Alloy 200 is shown in Table I [18]. It is particularly useful for maintaining product purity in the handling of foods, synthetic fibres and caustic alkalies, and also in structural applications where resistance to corrosion is a prime consideration. Other applications include chemical shipping drums, electrical and electronic parts, aerospace and missile components and rocket motor cases [18].

The microstructure typically exhibits a minor amount of non metallic inclusions, mainly oxides, which are unchanged by annealing [19]. Prolonged exposure in the temperature range of 425 to 540 C will allow any excess carbon to precipitate as graphite in a coarse grained material. This may lead to reduction in strength and ductility of the heataffected zone. Alloy 200 is approved as a material of construction under the ASME Boiler and Pressure vessels code [18]. Maximum allowable design stresses are based on tensile and yield strength. The room temperature mechanical properties of Alloy 200 are shown in Table II [10].

The basic corrosion characteristics of Alloy 200 are described in the references mentioned [1, 18, 19]. Only some pertinent features will be discussed here. In the electromotive series, nickel is more noble than iron and less so than copper. It does not discharge hydrogen from any of the common non oxidizing acids, so that a supply of some

TABLE I

CHEMICAL COMPOSITION OF ALLOY 200 (wt%) (FROM HUNTINGTON ALLOYS¹⁸)

Nickel 99.00 min	
Copper 0.25 max	
Iron 0.40 max	
Manganese 0.35 max	
Carbon 0.15 max	
Silicon 0.35 max	
Sulphur 0.01 max	

TABLE II

ROOM TEMPERATURE MECHANICAL PROPERTIES OF ALLOY 200 (FROM PRICE AND MORRIS¹⁰)

Temper	T.S MPa	Y.S 0.2% off set, MPa	Elongation in 2 in. %	Hardness HB
Hot-finished	414-586	103-310	55-35	90-150
Cold-drawn	448-758	276-689	35-10	140-230
Annealed	379-552	103-206	55-40	90-120

oxidizing agent such as dissolved air is required for corrosion. As a general rule, oxidizing conditions favor corrosion of nickel, while reducing conditions retard corrosion.

Alloy 200 can be used with unaerated sulfuric acid solutions at low or moderate temperature, although it is usually less resistant than nickel-copper alloys. In dilute solutions, the corrosion rate is increased by a high degree of aeration. Alloy 200 is moderately resistant to corrosion by hydrochloric acid, although its usefulness is limited to dilute solutions. Increasing temperature increases the corrosion rate of nickel in hydrochloric acid solutions as indicated by the test results in 5% acid shown in Figure. 1. Corrosion is also increased by the presence of air or oxygen.

Alloy 200 has limited usefulness in commercial phosphoric acid solutions because they usually contain impurities such as fluorides and ferric salts that accelerate corrosion. In pure, unaerated acid, corrosion rates are only a few mpy for all concentrations at atmospheric temperature. Alloy 200 should be used in nitric acid only in solutions of upto 0.5% concentrations at room temperature. It has excellent resistance to organic acids of all concentrations if aeration is not high. Alloy 200 in acetic acid of 0.1% concentration corroded at a rate of 10 mpy.

The outstanding corrosion resistance characteristic of Alloy 200 is its resistance to caustic soda and other alkalies. Ammonium hydroxide is an exception. The isocorrosion chart for nickel is shown in Figure. 2, is used as a general guide. Because of the presence of chlorates in caustic, the corrosion rates increase significantly. Every effort should be made to remove as much of them as possible. Oxidizable sulfur compounds also tend to increase the corrosivity of caustic to Alloy 200. Oxidizable acid salts such as ferric, cupric, and mercuric chlorides should be used with Alloy 200 only in low concentrations. The addition of such oxidizing salts as chromates, dichromates, nitrates, and peroxides to mineral acids may make them highly corrosive to nickel.



Figure 1. Corrosion of Alloy 200 in hydrochloric acid solution at 30 deg.C (From Friend¹⁹)



Figure 2. Isocorrosion chart for Alloy 200 in sodium hydroxide (From Friend¹⁹)

Pitting and Crevice Corrosion

Pitting is an example of highly localized corrosion. It is unusually destructive because perforation by a single pit can cause complete equipment failure. The attack is limited to extremely small areas of the metal surface while the remaining surface is relatively unaffected. Pits start at small points on the surface and enlarge with time. Surface finish often has a marked effect on pitting resistance. Pitting and localized corrosion are less likely to occur on a polished surface than on etched or ground surfaces and pits that form on a polished surface are larger and penetrate more rapidly than those on rough surfaces [20].

Metals and alloys such as nickel, iron and stainless steels have the ability to form thin, passive oxide films. These films are susceptible to either general or local breakdown in the presence of aggressive halide ions such as chlorides, bromides and hypochlorites. It has been argued that these ions can rupture or break the passive oxide film by adsorption on the surface, so that underlying metal is exposed to the aggressive environment at potentials high enough to cause pitting [22]. Another suggested mechanism involves direct incorporation of halide ions into the oxide film with a subsequent increase in pitting susceptibility [23]. The halide ion may however initiate passivity breakdown by simply interfering with local film repair. That is, the oxide may experience continuing local breakdown-repair events and the halide ion merely influences the efficiency of local repassivation. Figure. 3 shows the schematic sketch of three possible mechanisms for the pit initiation. The various theories and concepts used to explain the pitting corrosion are illustrated in the Appendix.

Nishimura [25] has studied the pitting corrosion of nickel in borate and phosphate solutions. From the linear relationship between time and total film thickness in the passive region it was proposed that a passive film formed in the solutions consists of two layers, an outer layer of Ni(OH)₂ and an inner layer of NiO. Thereby, the pit nucleation was assumed to be the period that continues until the inner layer is perforated by attack of Cl⁻



Figure 3. Schematic sketch of three possible initiation processes for pitting: (a) through incorporation of anions into the oxide, (b) through island adsorption of anions on the passive oxide, and (c) through tearing of the passive oxide (From Kaesche²⁴)

.

ions. This mechanism of film breakdown is same as that for iron, where as the kinetics of pit growth was much different from the iron.

Oxidizing metal ions with chlorides are aggressive pitters. Ferric, cupric, and mercuric chlorides are the amongst most aggressive of all pitting reagents [26]. These chlorides do not require the presence of oxygen to promote attack because their cations can be cathodically reduced. The cathodic reactions are

$$Cu^{2+}$$
 + 2e -----> Cu
Fe³⁺ + e ----> Fe²⁺

This is one reason for using ferric chloride widely, in pitting studies [26].

According to Evans [21], a corrosion pit is a unique type of anodic reaction which is an autocatalytic process. That is, the corrosion processes within a pit produce conditions which are both stimulating and necessary for the continuing activity of the pit. These conditions obviously are those that exist within a growing pit, namely, high chloride ion concentration and low pH. The anodic reaction during pitting is the solution of metal as ions

 $M ----> M^{+n} + ne$

where 'n' represents the charge of the metallic ion.

The immersion tests are the most common type of technique to evaluate the pitting corrosion. These tests provide direct comparison among various alloys, and correlate well with service experience. It is possible to establish the critical pitting temperature by this technique. The higher the critical pitting temperature is, the more resistant the alloy is to pitting corrosion [27, 29].

In general the crevice corrosion can occur when occlusion or crevice limits access of the bulk environment to a localized area of the metal surface. Localized environmental changes in this stagnant area can result in the formation of acidic/high chloride conditions that may result in the initiation and propagation of crevice corrosion of susceptible alloys. Crevices can be classified into two classes: (a) naturally occurring, that is those created by deposits, sediments, debris etc., and (b) man-made, that is those created during manufacturing, fabrication, assembly, or service.[49].

The initiation of crevice corrosion is highly dependent on many factors - alloy composition, crevice geometry, and bulk chloride content. The geometry of a crevice can be described by the dimensions of crevice gap and crevice depth. Crevice gap is identified as the width or space between the metal surface and the crevice former. Crevice depth is the distance from the mouth to the center or base of the crevice [50].

LME and HE

Many metals and alloys exhibit embrittlement when exposed to other liquid metals. The general requirements for this phenomenon to occur appear to be

(i) a tensile stress

(ii) a pre existing crack or some amount of plastic deformation, so that dislocation pileups against an obstacle can occur, resulting in concentrated tensile stress across the potential fracture plane, and

(iii) adsorption of the embrittling species at the obstacle.

Limited mutual solubility is required, since too great a solubility may result in dissolution, with the possibility of crack blunting. Little tendency to form intermetallic compounds is also a requirement since this is a characteristic of high bonding strength. LME occurs more readily in an alloy as the stacking fault energy (SFE) is lowered [28].

Some alloys fail under stress in corrosive conditions because of entry of hydrogen atoms into the alloy lattice. This phenomenon is called HE. The hydrogen appears to have no effect upon the elastic modulii of the material. At very low temperatures, embrittlement by hydrogen does not occur because the diffusion rate of hydrogen is low at lower temperatures [9]. The cracks are mainly intergranular and start where the surface is subjected to the highest tensile stress. One outstanding feature of the HE is that it is only detectable at low strain rates. Since it is likely that the hydrogen in the lattice diffuses to the deformed region at the tip of the crack, a high strain rate does not allow the necessary time for this movement to occur.

There is a major distinction between SCC and HE. SCC depends upon anodic dissolution for atleast a part of the propagation process, and can be avoided by cathodic protection. HE in contrast, is induced by cathodic polarization, since this promotes the production of hydrogen.

Lynch [30] demonstrated that the fractographies, and grain size effects of HE and LME are often similar and pointed that the fracture mechanism is the same. Also, several authors made a suggestion that the same mechanism may be responsible for HE, LME as well as SCC [31, 32, 33]. While investigating the embrittlement in magnesium alloy, Lynch and Traveena [34], have come to a conclusion that adsorption of either adatoms or hydrogen is responsible for the embrittlement cracking.

An investigation was performed by Price and Good [4], using the slow strain rate tests, to determine whether nickel and typical nickel base alloys were susceptible to embrittlement by liquid mercury at room temperature. Results indicated that all the alloys were embrittled by mercury. The fracture mode was governed by the strain at which cracking initiated with lower values favoring intergranular separations. Some alloys showed a progression from IG to TG to MVC across the cross section, the latter failures occurring at higher strain levels. The relative embrittlement of the alloys did not correlate with the mechanical properties or the SFEs, but is perhaps related to composition, for example, the alloys higher in iron content were less effected.

The fatigue life times and fractography were compared for nickel and nickel-base alloys at room temperature in alternating tension in the environments of air and liquid mercury [5]. It was found that the fatigue life was always less in mercury and that a different fracture mode resulted. The alloys 200, 600, 800, and 825 that did not show IG fractures in the slow strain rate tensile tests, did so under fatigue testing. A generalized

crack propagation sequence in mercury was identified beginning with IG cracking but transferring eventually to TG modes.

Traylor [9] used slow strain rate tests and fatigue tests to explore hydrogen embrittlement of Alloy 200 at room temperature. It was found that only dynamic charging with hydrogen led to embrittlement. There was no loss of tensile strength in the embrittled material. A crack propagation sequence, beginning at the surface, was identified as IG cracking, non-crystallographic TG cracking, crystallographic TG cracking, and then MVC. It was deduced that HE must be substantially a surface phenomenon.

Stress Corrosion Cracking

SCC includes any combination of corrosion and static tensile stress that leads to failure by cracking. The stresses required to cause SCC are small, usually below the yield stress of material. Pickering and Swann [35] found that corrodents that are effective in producing SCC of metals generally produce a film over most of the surface. These films may be passivating layers, tarnish films or dealloyed layers. Only under certain critical conditions can SCC occur. These conditions include elctrochemical, mechanical, and metallurgical factors that must exist simultaneously. A change in any of these three factors is adequate for eliminating SCC [39].

The important electrochemical factors include oxidizing potential, pH, impurity concentration, and temperature. The mechanical factors include stress, stress intensity, and strain rate. The essential metallurgical factors include localized micro chemistry, bulk composition, deformation characteristics, and yield strength. SCC has one of the characteristics of brittle fracture. In certain materials, cracking is transcrystalline, in others, it may be transcrystalline or intercrystalline, while in a third group, it is primarily intercrystalline [37].

Until recently, it was thought that the pure metals were immune to SCC. However, it has been shown that pure metals are susceptible to SCC [38]. The tensile specimens of

copper single crystals (99.99% pure) tested in 1M NaNo₂ at 25 C showed surface cracks of 300 μm deep and are macroscopically linked along slip planes.

There are a number of mechanisms that account for SCC. No single mechanism is adequate to describe SCC in the variety of methods that has been observed. According to Dix and his coworkers [36], a prerequisite for SCC is the existence of a localized anodic path in the material. Thus in the presence of a corrosive environment and a tensile stress, a galvanic cell is set up in which the anodic path is preferentially attacked. The base of the resulting corrosion crevice then becomes the site of the stress concentrations, and they were thought to cause the metal to tear apart by mechanical action. This tearing action exposes fresh metal, so that acceleration occurs in this region. This in turn leads to further stress concentration and further tearing of the metal. Thus, cracking propagates by cycles of accelerated corrosion and tearing of the metal.

Pugh [40] has discussed the various mechanisms proposed to explain the SCC in metals and alloys. Figure. 4 shows a schematic of film-rupture mechanism. The passive film is ruptured by slip exposing the metal for the formation of tubular corrosion pits. The ductile rupture of a slot weakened by tubular pits will lead to cracking. The tarnish rupture mechanism proposed for alpha brass has been illustrated in Figure. 5. The first stage involves the formation and rupture of the tarnish (a-b). An essential feature of the theory is that the crack does not propagate into brass substrate, but becomes blunted by plastic deformation (c). Fresh brass is then exposed to tarnishing solution, allowing the process to be repeated (d-f). Cracking thus proceeds in a discontinuous fashion, producing fracture surface shown in (g).

In materials having complex slip systems or high stacking fault energies (SFE), cracks will most probably follow intercrystalline paths. In materials of low SFE, short range order and having planar array of dislocations after plastic deformation, cracks may follow transcrystalline or intercrystalline paths, depending upon the corrodent and the extent of plastic deformation [37]. Copson [41] has reported that by increasing the nickel









content from 8% to 40% in austenitic stainless steels, the alloy is rendered immune to SCC in boiling 42% MgCl₂ solution.

Previous SCC Studies on other Nickel-Base Alloys

Several experiments have been carried out on Alloy 400 to determine it's susceptibility to SCC at room temperature. Everhart [11] has carried out immersion tests on Alloy 400 in a wide range of environments. Based on the test results, she selected three environments - ammonium persulfate (0.175M), ammonium hydroxide (29%), and hydrofluoric acid for SCC tests. The tests were conducted at relatively slower strain rates varied between 3.0×10^{-5} to 1.2×10^{-6} s⁻¹. SCC has been observed in all the environments with varying degrees. She has observed that by increasing the strain rate, a cracking sequence of IG to TG to MVC occurred.

Deardorff [42] has demonstrated pitting attack of Alloy 400 in 0.0125M to 0.4M ammonium persulfate solutions. It was reported that 0.4M was too high a concentration and yielded overall general attack. Also, IG SCC was observed for Alloy 400 in 0.1M ammonium persulfate at a strain rate of $3.75 \times 10^{-6} \text{ s}^{-1}$. It was suggested that tests should be conducted at even slower strain rates to obtain completely brittle fracture with no plastic deformation at all.

Lu [13] has carried out immersion tests on Alloy 400 in ammonium persulfate (0.001M to 0.05M), and ferric chloride (0.001M to 0.1M) solutions. the results showed that even at 0.005M concentration of ammonium persulfate appreciable pitting corrosion has occurred. Slight pitting attack has observed in 0.001M ferric chloride solutions. He has also reported crevice attack at the bottom of samples in ammonium persulfate solutions. SCC tests were conducted in 0.03M and 0.01M ferric chloride and 0.05M and 0.01M ammonium persulfate solutions. All the tests showed SCC to different degrees.

Based on the above test results, Choday [43] has found the limiting concentrations for pitting attack of Alloy 400. It was reported that no pitting has occurred at 0.001M

concentration in both ferric chloride and ammonium persulfate solutions. The results of SCC tests revealed that considerable amount of SCC has occurred at a concentration of 0.005M in both the solutions. However, the corrosion fatigue tests did not show any SCC in Alloy 400. He also concluded that pits initiated during chemical polishing did not grow in the subsequent immersion tests.

SCC in Alloy 600 has been investigated by Hussen [14]. The immersion tests were carried out in ferric chloride solutions at concentrations of 0.01M to 0.1M. He has also studied the effect of temperature on pitting behavior of Alloy 600. The results indicate that pitting corrosion has increased with the concentration and temperature. Because of the transpassive behavior of Alloy 600, corrosion resistance increases up to a specific temperature in specific concentrations. Also the sensitization heat treatment affected the pitting behavior considerably. The sensitized samples showed more pits than the unsensitized samples because of the precipitation of chromium carbides which leaves the grains lacking chromium and hence less corrosion resistance. The SCC test results showed a tremendous amount of SCC in 0.1M ferric chloride solutions. In sensitized condition two kinds of microstructures have been observed, IG cracking in the shoulders and microvoids in the neck region. Consequently, the fracture is assumed to start by the penetration of solution from all sides which created IG cracking in the shoulders and ended in the middle which created the microvoids in the neck region. The grains and grain boundaries showed some pitting attack. In unsensitized condition, side cracking which is similar to TG cracking on one side of the specimen and microvoids on the rest of the sample. There was no pitting on the specimen surface.

Zaheer [15] has studied the pitting and SCC behavior of Alloy 800. He has conducted a wide range of pitting tests in ferric chloride, ammonium persulfate, and cupric chloride solutions at fairly higher concentrations. The results of pitting tests indicate that basically pit initiation is dependent upon surface finish, alloying elements, heat treatment including the degree of sensitization and film formation. The titanium nitride particles

behave cathodically causing preferential attack on the matrix. The higher the degree of sensitization the greater was its inclination towards pitting. The unsensitized samples are nearly immune to pitting attack. It was observed that electropolished samples showed more pits than mechanically polished samples, but the pits on the latter are usually large.

Zaheer has also demonstrated that a linear relationship exists between pitting behavior and solution concentration and time of immersion. From the morphology point of view, the interior of the pit is composed of shiny, crystalline facets. Alloy 800 is prone to crevice corrosion in ferric chloride solutions. This has been discussed in the subsequent chapters. The cupric chloride and ammonium persulfate solutions showed only slight pitting attack. The SCC tests on indented samples showed no cracking. Also the tests by SST did not show any SCC in 0.4M ferric chloride solutions. He has also conducted LME tests in liquid mercury and corrosion fatigue tests in 0.4M ferric chloride. Some embrittlement of Alloy 800 has been reported in corrosion fatigue tests.

CHAPTER III

PROPOSED INVESTIGATIONS

The objectives of this investigation are to demonstrate the pitting behavior of Alloy 200 in selected environments and to explore any stress corrosion cracking at room temperature.

The proposed experiments will be carried out in the following sequence:

- (a) Immersion tests for exploring the pitting behavior
- (b) SCC tests on pre-stressed samples
- (c) SCC tests by SST technique

The test samples will be mechanically polished to $0.05 \,\mu\text{m}$ finish on both top and bottom surfaces. The side surfaces are not polished and they will be in as-received condition. Some of the samples will be chemically polished to study the effect of surface condition on pitting behavior.

The first experimental stage involves performing immersion tests. The environments chosen for immersion tests are Hydro chloric acid, Ferric chloride, Cupric chloride, and Ammonium persulfate. The solutions are selected based on the corrosion rates of Alloy 200 in these environments. It is desired to have only light or localized attack leading to slight pitting since, this is the required condition for the stress corrosion cracks to initiate [29]. Also, these are the active environments (with the exception of hydrochloric acid) which caused pitting of other nickel-base alloys at room temperature.

Initially, some immersion tests will be carried out in Hydro chloric acid to study the general corrosion behavior of Alloy 200. Also, these samples can be used for comparison purposes in the analysis of pitting test results. The samples will be immersed in different

concentrations of the solutions for a predetermined period of time to study the time dependency on pit initiation and growth.

Based on the results of immersion tests the test parameters for SCC tests will be selected. These parameters include type of solution, concentration, and strain rates. The strain rates will be chosen in such a manner that only slight pitting attack should occur. The SCC tests will be performed initially on pre-stressed samples and then on waisted tensile samples. All the tensile samples will be heat treated for obtaining the desired grain size. The photographs of interesting samples in immersion tests and SCC tests will be taken for analysis.

These experimental results will be compared with that of Alloy 400, Alloy 600, and Alloy 800 which were already investigated in complimentary studies at OSU [11, 13, 14, 15, 42, 43]. The conclusions will be drawn based on the analysis of these results.

CHAPTER IV

EXPERIMENTAL PROCEDURE

Immersion Tests

Sample Preparation

Round discs of 0.5x0.5 inch were ground through a 600 grit finish and mechanically polished down to 0.05 μ m on both top and bottom surfaces. The size of specimen and testing procedure were adopted from ASTM specifications [44, 45]. Finally, the samples were rinsed in water, flooded with methanol, and dried in blowing warm air.

Some samples were chemically polished in an 85 C solution [46] containing

30 ml nitric acid

10 ml sulphuric acid

10 ml orthophosphoric acid

50 ml glacial acetic acid

The samples were immersed in the solution for a minimum period of thirty seconds and a maximum of sixty seconds. The samples are then rinsed in water and methanol and warm air dried.

Test Procedure

The solutions selected for immersion tests are:

(a) Hydrochloric acid with concentrations of 5% and 10%

(b) Ferric chloride with concentrations of 0.04M, 0.02M, 0.004M and 0.002M

(c) Cupric chloride with concentrations of 0.293M, 0.176M, 0.0586M, 0.029M, and 0.006M

(d) Ammonium persulfate with concentrations of 0.219M, 0.134M, 0.044M, and 0.022M(e) Hydrofluoric acid

Alloy 200 is resistant to most alkalies, but it is not resistant to aerated ammonium hydroxide solutions [19]. To verify this, one immersion test was carried out in 80% ammonium hydroxide and two tests in aerated ammonium hydroxide solution. The alloy was tested in chloride environments, and ammonium persulfate due to its tendency towards corrosion attack by oxidizing acid salts.

The addition of 10% hydrochloric acid to any of the above mentioned environments is expected to increase the tendency towards general attack. Two immersion tests were carried out in ferric chloride and cupric chloride with the addition of 10% hydrochloric acid. Previous studies on Alloy 400 with hydrofluoric acid have shown pitting attack [11]. An attempt has been made to examine the behavior of Alloy 200 in the same concentration of hydrofluoric acid.

To study the effect of surface condition some samples were chemically polished. The chemical polishing was carried out at different temperatures within the specified range of 85-95 C and time periods. The polished samples were examined under a microscope to select the optimum polishing conditions for subsequent immersion tests. Six immersion tests were carried out with chemically polished samples in ferric chloride, cupric chloride, and ammonium persulfate solutions. The solution concentrations and test durations are similar to that of immersion tests by mechanically polished samples for comparison purposes. The observations of these tests will be compared with that of mechanical polishing samples to determine the effect of surface condition on pitting behavior of Alloy 200.

Individual samples were placed in petri dishes containing 50-60 ml of the appropriate solutions. The solutions will be in stagnant condition all the time. After a

predetermined time period, the samples were taken out, thoroughly cleaned with water, ultrasonically cleaned in methanol, and warm air dried. Before cleaning the sample, the appearance of surfaces and other observations were recorded.

The cleaned samples were examined under the Bausch & Lomb Zoom microscope at 70X and Olympus optical microscope at 200X and 800X. Some photographs were taken for analysis. The most significant samples were examined and photographed under a Jeol JSM-35 Scanning Electron Microscope (SEM).

Stress Corrosion Cracking Tests

Tests on Pre-stressed samples

Initially, the SCC tests were carried out on pre-stressed samples with the immersion test procedures. After polishing, the top surface of the sample was indented by a 3/16 inch diameter ball under a load of 7000 pounds. The samples were then immersed in the selected solutions at different concentrations and time periods. After the predetermined time period the samples were cleaned and observed under optical microscope for any stress corrosion cracking.

Slow Strain Rate Tests

The tensile specimens were waisted with a 0.25 inch minimum diameter that gradually increases to 0.5 inch at the shoulders at the end of each gauge length. Figure. 6 shows the geometry of a tensile specimen. An advantage of this geometry is the strain gradient, hence a damage gradient, along the gage length, which maximizes the information obtained from each test. The samples were heat treated for 1 hour at 750 C, furnace cooled for 4 hours and air cooled to room temperature. The approximate grain size obtained by this annealing treatment is $35 \,\mu$ m. After heat treatment, the samples were finished to 600



Figure 6. Geometry of Tensile specimen (From Zaheer¹⁵)

grit and polished to $0.05 \,\mu\text{m}$ by alumina to get a smooth surface free of machining grooves and longitudinal scratches.

All SCC tests were carried out on MTS machine at room temperature in ferric chloride, cupric chloride, and ammonium persulfate at selected concentrations. Figure. 7 shows the arrangement of tensile specimen with environment chamber between the grips. Only the polished surface of specimen will be exposed to the solutions. The tests were run under stroke control which was set at 100% and 20% of full stroke. The corresponding ram speeds were varied between 1×10^5 and 5×10^5 seconds.

After the failure, the samples were thoroughly rinsed in water and ultrasonically cleaned in methanol and warm air dried. All samples were observed under a Bausch & Lomb stereoscopic zoom microscope at 70X. The selected samples were sectioned for examination under a Jeol model 35 SEM. All interesting features were recorded and photographed for analysis.


Figure 7. Schematic of specimen arrangement on MTS machine (From Everhart¹¹)

CHAPTER V

EXPERIMENTAL RESULTS

Immersion Tests

Immersion Tests in Ferric Chloride Solutions

The observations of pitting tests on Alloy 200 are tabulated in Table III. These results indicate that the concentration of ferric chloride has a direct consequence on the pitting attack. For example, the immersion tests at 48 hours in 0.04M, 0.02M, 0.004M and 0.002M have shown general attack in decreasing order. Refer Figure. 8. It indicates that the 48 hours duration was long enough to cause general attack at these concentrations. But the degree of general attack has decreased proportionately with solution concentration. When the pitting attack is dominated, a small number of big size pits were observed. The pitting attack occurs before the general corrosion is observed.

When the time of immersion is reduced to 24 hours, many small and big size pits were observed with slight general attack at 0.04M concentration. Figure. 9 shows the nature of attack in 0.04M concentration. The size and distribution of pits seems to be directly related to the solution concentration. The number of pits and depth of pits is favored by definite solution concentration. At 12 hours immersion, the general attack is eliminated at all the concentrations tested. The pitting attack is gradually diminished from 0.04M to 0.002M concentration. Refer Figures. 10 and 11. A graph has been plotted (Figure.12) to show the effect of solution concentration on pitting attack at 24 hours duration. It shows that pitting attack is gradually decreased with increasing solution

Sample #	Concentration	Duration hours	Observations
M1	0.04M	48	Shiny appearance, general corrosion with many small pits on top, side face is dull and has general attack, grain etched, pits at the edges are deep and shallow at the center on bottom
M5	0.04M	24	Many small pits on top, slight general attack on sides, on bottom general corrosion and pitting attack with slight grain etching
M15	0.04M	12	Dark brown patches on top, more number of small size pits on bottom than on top, and light grain etching, some small size pits on side
M3	0.02M	48	Many small size pits on both top and bottom, very few on sides, light grain etching
M7	0.02M	24	Many small pits on both and bottom, and a few on sides, and light grain etching
M16	0.02M	12	Few small size pits on both top and bottom, partial grain etching
M4	0.004M	48	Some small and big size pits on both top and bottom, only the bottom has been etched
M8	0.004M	24	Some small size pits on both top and bottom, only the bottom has been grain etched
M17	0.004M	12	Slight pitting attack and no grain etching on top, some big size pits and partial etching on bottom
M31	0.002M	48	Dark brown & light green patches and slight pitting attack on top, some big size pits and partial grain etching on bottom
M32	0.002M	72	Top surface is shiny with few small pits, bottom is lightly etched with many pits

IMMERSION TESTS IN FERRIC CHLORIDE SOLUTIONS

Sample #	Concentration	Duration hours	Observations
M 41	0.002M	12	Few small round pits on top and bottom, only light grain etching on bottom
M23	0.004M+10%Hcl	24	Some small size pits on both top and bottom, top is shiny, no grain etching
M24	0.02M+10%Hcl	24	Few pits on top, some general attack and small pits on bottom, dark grain etching

TABLE III (Continued)

Figure 8. The Corrosion attack of Alloy 200 in 0.04M Ferric chloride solution for 48 hours shows General attack and different sizes of pits (180X)

Figure 9. The Corrosion attack of Alloy 200 in 0.04M Ferric chloride solution for 24 hours shows some general attack and pitting (180X)



Figure 10. The Pitting attack of Alloy 200 in 0.004M Ferric chloride solution for 12 hours shows few small size pits (180X)

Figure 11. The Pitting attack of Alloy 200 in 0.002M Ferric chloride solution for 12 hours shows some small size pits (180X)

.







concentration. At higher concentrations, the general corrosion attack will be dominated with increasing duration.

The graph (Figure.13) shows the effect of time of immersion on pitting attack for 0.004M solution concentration. The effect of addition of 10% hydrochloric acid has increased the tendency for general attack at 0.02M concentration, but not at 0.004M.

In summarizing the results of immersion tests in ferric chloride, Alloy 200 has shown general attack and pitting attack in all the concentrations tested. The 0.04M concentration seems to be a upper limit to cause pitting. The concentrations below 0.002M might experience pitting with increasing duration of immersion. The pit shape varies from round to irregular. At lower concentrations, many of the pits have round shape and they were distributed all over the surface. The pits in higher concentrations, have both round and irregular shape and were randomly distributed. Some irregular shaped pits have undercutting. Compared to top and bottom surfaces, the attack is less on side surfaces. The side surface is not polished and also because of the slant surface, the pitting is not clearly visible. The etching was observed on sides at higher concentrations.

Immersion Tests in Cupric Chloride solutions

The observations of pitting tests an Alloy 200 are tabulated in Table IV. These results indicate that at higher concentrations of the solution, thick and adherent green deposits have formed on the sample. Big size pits were observed underneath these deposits. It is observed that cupric chloride seemed to be more detrimental for pitting corrosion resistance of Alloy 200. Also, on the bottom of the specimen, crevice attack has been observed at all concentrations except at the lower limit of 0.006M. The extent of crevice attack is proportional to the concentration of solution and time of immersion. When the crevice attack occurs on bottom, the top and side surfaces were less affected. The difference in attack is due to the formation of anode and cathode on bottom and top



TIME OF IMMERSION IN HOURS

Figure 13. Effect of Time of immersion in 0.004M Ferric chloride

.

IMMERSION TESTS IN CUPRIC CHLORIDE SOLUTIONS

Sample #	Concentration	Duration hours	Observations
M11	0.293M	24	Thick green deposits on all the surfaces, many large deep pits and general attack on top and sides, small pits and severe crevice attack on bottom around the edge, grain etching on all the surfaces
M14	0.293M	12	Thick green deposits on all the surfaces, many small and big deep pits on both top and bottom, slight pitting attack on sides, crevice attack on bottom and grain etching
M10	0.176M	24	Thick green deposits on top and bottom, many small and big size pits on both top and bottom, light etching and slight attack on sides, crevice attack on bottom and grain etching
M13	0.176M	12	Thick green deposits on top and bottom, many small and big size pits on both top and bottom, slight crevice attack and grain etching on bottom
M2	0.0586M	48	Light green deposits, few small and big deep pits on top, slight attack on sides, and on bottom slight crevice attack and grain etching is observed
M6	0.0586M	24	Dark green & brown patches and few small size pits on top, many small and big deep pits near edge on bottom, grain etching only on bottom
M12	0.0586M	12	No pitting attack on top and sides, some small size pits and partial etching on bottom
M18	0.029M	24	Some small size deep pits on top, no attack on sides, on bottom many small size pits and partial grain etching is observed
M19	0.029M	12	Some small deep pits are observed on top and is lightly etched, many small size pits on bottom

Sample #	Concentration	Duration hours	Observations
M42	0.029M	72	Many small deep pits on top and bottom, light etching and no crevice attack on bottom
M33	0.006M	48	Many small size pits on both top and bottom, grain etching and no crevice attack on bottom
M34	0.006M	72	Many small size deep pits on top, few irregular shaped pits and grain etching on bottom
M43	0.006M	12	Very few small shallow pits on both top and bottom, and no etching
M25	0.0586M+10%Hcl	24	Some general attack, many small pits and grain etching
M26	0.029M+10%Hcl	24	Slight general attack and small size pits, dark etching, and no crevice attack

.

TABLE IV (Continued)

respectively. Crevice attack is not observed in ferric chloride solutions. At higher concentrations, the pits observed were bigger and deeper than in ferric chloride solutions.

The Figures. 14 and 15 show the severe pitting and general attack at 0.279M concentration at 24 hours immersion. Many big and deep pits have joined together to form big cavities. The green deposits were visible inside and outside the cavities. The bottom of the same specimen showed severe crevice attack around the rim. The deep pits were observed only on top but on the bottom the general attack has been dominated. Fig.16 showed the same observations but at 12 hours of immersion. It indicates that 0.279M concentration is highly detrimental for pitting as well as general corrosion resistance of Alloy 200. It should be noted that because of severe corrosion attack the top and bottom surfaces have porous type structure. The deep pits were covered by green deposits.

At 0.176M concentration also similar type of corrosion attack has been observed but to a lesser degree than 0.279M concentration. Crevice attack was observed on bottom surface in either case. Refer Figures 17 and 18. When the concentration of the solution is reduced to 0.0586M, only small number of deep pits were observed on top surface without any general attack. But on bottom surface, general corrosion with slight crevice attack has been observed. It should be noted that at this concentration the corrosion attack is less severe when compared to 0.279M and 0.176M. Also, the green deposits were only light and not adherent. Figure. 19 shows the corrosion behavior of Alloy 200 at 0.0586M.

A graph (Figure. 20) has been plotted to show the effect of time of immersion on pitting attack at 0.0586M concentration. At higher concentrations, the pits formed were less in number but very big in size and depth. Many number of small size pits were observed at lesser concentrations. Also, at the concentration of 0.176M and above, the pits have joined together to form cavities. Hence, it was not always the case to have more number of pits with increasing concentration. The increasing concentration might effect the pit size and distribution, but not the number of pits in some situations. At the same concentration of the solution, if any pits are formed, the number of pits may increase with

Figure 14. The Pitting attack of Alloy 200 in 0.293M Cupric chloride solution for 24 hours shows many big and small size deep pits on top surface (21X)

Figure 15. The bottom surface of the above sample showing Pitting and severe Crevice attack (18X)



Figure 16. The Pitting attack of Alloy 200 in 0.293M Cupric chloride solution for 12 hours shows many pits and some Crevice attack on bottom surface (18X)

.

Figure 17. The Pitting attack of Alloy 200 in 0.176M Cupric chloride solution for 24 hours shows many small size pits and slight Crevice attack (13X)



Figure 18. The Pitting attack of Alloy 200 in 0.176M Cupric chloride solution for 12 hours shows few small size pits and slight crevice attack on bottom surface (14X)

Figure 19. The Pitting attack of Alloy 200 in 0.0586M Cupric chloride solution for 12 hours shows few big and small size pits on top surface (180X)







TIME OF IMMERSION IN HOURS

Figure 20. Effect of Time of immersion in 0.0586M Cupric chloride

the increasing time of immersion. Figure. 21 shows the effect of concentration on pitting behavior.

The general attack was totally absent on top surface at 0.029M concentration. Only small number of deep pits and some pit initiation sites have been observed. Also, the general attack is limited to only central portion of the bottom surface and crevice attack is very limited. Figures. 22 and 23 explain the nature of attack at 0.029M.

At 0.006M solution concentration, the crevice attack was not observed in any of the samples. Also, the general attack was very minimal on bottom. A small number of shallow and deep pits and many pit initiation sites were observed on both the surfaces. This concentration seems to be the lower limit to cause pit initiation at 12 hours of immersion. Pits may occur in still diluter solutions with increasing duration of immersion. Figure. 24 shows the type of attack observed at 0.006M solution concentration. The addition of 10% hydrochloric acid has increased the tendency for general attack to a great extent. Refer Figure. 25. In case of ferric chloride solutions, this effect is not much pronounced.

In a summary, the cupric chloride solution is found to be more detrimental to the pitting corrosion resistance of Alloy 200. Even at low concentrations pitting has occurred within short durations. The pits have more regular shape on top than on bottom surfaces. Round and deep pits were observed on top surfaces and they were distributed more uniformly all over the surface. The pits on bottom have irregular shape and undercutting and they were distributed mostly around the edge of the surface. The center portion is either unaffected or have some general attack. The side surfaces are less affected than top and bottom. Alloy 200 is susceptible to crevice attack in cupric chloride solutions.

Immersion Tests in Ammonium Persulfate Solutions

The observations of pitting tests on Alloy 200 in Ammonium persulfate solutions



Figure 21. Effect of Concentration on Pitting Behavior in Cupric chloride at 24 hours duration

Figure 22. The Pitting attack of Alloy 200 in 0.029M Cupric chloride solution for 24 hours shows small size pits on top surface (180X)

Figure 23. The Pitting attack of Alloy 200 in 0.029M Cupric chloride solution for 72 hours shows few small size deep pits on top surface (180X)



Figure 24. The Pitting attack of Alloy 200 in 0.006M Cupric chloride solution for 12 hours shows few deep pits on top surface (180X)

Figure 25. The Corrosion attack of Alloy 200 in 0.029M Cupric chloride and 10% Hydro chloric acid shows severe general corrosion and few pits (180X)





are tabulated in Table V. These results indicate that Alloy 200 is susceptible to pitting and crevice attack in ammonium persulfate solutions. At 0.219M concentration for 24 hours immersion, many big and small size deep pits have occurred on top surface. On bottom face, the general attack is dominated with slight crevice attack. Refer Figure. 26. The extent of attack at this concentration is comparable to that of 0.176M cupric chloride solution at 24 hours.

When the solution concentration is reduced to 0.134M, the corrosion attack is similar to that of at 0.219M, but at slightly lesser degree. Some shallow pits and crevice attack has occurred on bottom face. Figure. 27 shows the nature of attack at 0.134M. At 0.044M concentration, the pits are not very deep as observed for 0.219M and 0.134M, but the general corrosion has occurred on both faces. For 24 hours immersion, a slight crevice attack is observed. Refer Figure. 28.

The crevice attack is not observed at 0.022M concentration. Also, the pits observed were shallow on top face. The bottom face is subjected to general corrosion, as the time of immersion is increased. These observations indicate that 0.022M concentration is lower limit to initiate pitting in 24 hours in Alloy 200. Figure. 29 shows the pitting attack at 0.022M concentration.

In a summary, Alloy 200 is susceptible to pitting and crevice attack in ammonium persulfate solutions. The extent of crevice attack is limited to 0.044M and higher concentrations. Except some color patches, no deposits have been formed on the sample. Most of the pits have irregular shapes on top and distributed uniformly. The pits on bottom distributed mostly around the edge of the surface. Compared to ferric chloride solutions, the corrosion attack is much severe in ammonium persulfate solutions.

Follow up immersion tests

The observations of immersion tests in ammonium hydroxide and hydrofluoric acid

IMMERSION TESTS IN AMMONIUM PERSULFATE SOLUTIONS

Sample #	Concentration	Duration hours	Observations
M20	0.219M	24	Many big and small size deep pits on top, severe general attack and slight crevice attack and grain etching is observed on bottom
M21	0.134M	24	Some white patches with small size deep and shallow pits on top, severe general attack, slight crevice attack and grain etching on bottom
M22	0.044M	24	Many big size pits on both top and bottom, slight general and crevice attack on bottom, both surfaces are dark etched
M45	0.044M	12	A large number of small size pits and partial etching on both surfaces, slight general and no crevice attack on bottom
M35	0.022M	48	Some small size pits on top, clean rim, general attack and many small pits on bottom
M36	0.022M	72	Many small pits on top, clean rim, severe general attack and few pits observed on etched bottom
M44	0.022M	24	Green and brown patches on top, some small size pits on both top and bottom, partial grain etching

Figure 26. The Corrosion attack of Alloy 200 in 0.219M Ammonium persulfate solution for 24 hours shows General corrosion and Crevice attack on bottom surface (18X)

Figure 27. The corrosion attack of Alloy 200 in 0.134M Ammonium persulfate solution for 24 hours shows General Corrosion and slight Crevice attack on bottom surface (14X)



Figure 28. The corrosion attack of Alloy 200 in 0.044M Ammonium persulfate solution for 24 hours shows Pitting attack leading to General corrosion and slight Crevice attack (180X)

Figure 29. The Pitting attack of Alloy 200 in 0.022M Ammonium persulfate solution for 48 hours shows small size deep pits on top surface (180X)



are tabulated in Table VI. The results indicate that Alloy 200 is immune to pitting attack in unaerated ammonium hydroxide solutions. When the tests were carried out in aerated solutions, some irregular shaped deep pits and many pit initiation sites were observed. Refer Figure. 30. No general attack is observed upto 48 hours immersion. This indicates that air saturated ammonium hydroxide solutions are detrimental to the pitting corrosion resistance of Alloy 200. The tests were carried out at very high concentrations.

It was observed that Alloy 200 is susceptible to pitting attack in HF solution. Some irregular shaped pits and many pit initiation sites were observed in 48 hours immersion. Similar type of attack has been observed with Monel 400 in HF acid solution [11]. Figure. 31 shows the pitting attack of Alloy 200 in HF acid solution.

Effect of Surface condition

The observations on chemically polished samples are shown in Table VII. chemical polishing induces some pitting during the polishing operation. When the samples were immersed in chemical polish solution at room temperature, some inclusions and pit initiation sites were observed. No polishing action took place under these conditions. At 95 C many small pits and blisters were observed. This attack was severe when the sample was immersed for 60 seconds (Figure. 32). The blisters appear like surface projections. The grain boundaries were clearly visible in all the polished samples. Also, it should be noted that during polishing, a vigorous bubbling action takes place in the solution and giving out lot of fumes. Some of the gas bubbles might have been trapped on the sample surface and formed blisters.

The surface of mechanically polished sample shows no imperfections such as blisters, inclusions or pits. It means that the surface condition of mechanically polished samples was better than chemically polished ones. Hence, it can be expected that the corrosion attack would be less severe in case of mechanically polished samples.

Sample #	Concentration	Duration days	Observations
M27	80% NH4OH Unaerated	4	Both top and bottom surfaces are shiny and unaffected
M48	Aerated 100% NH4OH	2	Shiny surface, some irregular shaped d deep small pits and inclusions are observed, no general attack
M49	Aerated 80% NH4OH	2	Shiny surface, some small size pits are visible, no general attack
M50	26% HF	2	Shiny surface, no grain etching, many pit initiation sites and irregular small size pits

FOLLOW UP IMMERSION TESTS

Figure 30. The Pitting attack of Alloy 200 in Aerated 80% Ammonium hydroxide for 48 hours shows some small size pits on top (180X)

Figure 31. The Pitting attack of Alloy 200 in 26% Hydrofluoric acid for 48 hours shows small deep pits on top (180X)


Sample #	Temperature deg.C	Duration seconds	Observations
PT1	R.T	30	Shiny surface, no etching, some inclusions and few small pit initiation sites are visible, no polishing
PT2	R.T	60	Shiny surface, no etching, some inclusions and more number of small size pit initiation sites, no polishing
PT3	95	30	Slightly dull surface, light etching, many small pits
PT4	95	45	Dull surface, light grain etching, many small and big round pits all over the surface
PT5	95	60	Dull appearance, severe grain attack, many big round pits, and some small pits all over the surface

OBSERVATIONS AFTER CHEMICAL POLISHING

The observations of immersion tests on chemically polished samples are tabulated in Table VIII. The results indicate that chemical polishing has enhanced the corrosion attack significantly. For example, comparing samples M5 and CP1 (Figures. 9 and 33), the extent of general attack is less severe in case of mechanically polished sample. The pits are clearly visible in Figure. 9 due to light etching. When the samples M18 and CP2 are compared (Figures. 22 and 34), the extent of pitting attack is similar on top surface, but the presence of blisters is clearly seen in Figure. 34. Both bottom surfaces have general attack only at the center of samples. The comparison of samples M22 and CP3 (Figures. 28 and 35), indicates that pits initiated during chemical polishing did not grow into fully developed pits during subsequent immersion tests. Figures. 36, 37, and 38 show the nature of attack in dilute solutions but at longer durations. It indicates that chemical polishing has enhanced the corrosion attack significantly.

In a summary, the observations on chemically polished samples indicate that some pits were initiated during chemical polishing and they did not grow in subsequent immersion tests. The chemical polishing has enhanced the tendency for general attack to some extent. The tendency for crevice attack is not affected significantly by chemical polishing. The presence of pit initiation sites and blisters were observed in all the chemically polished samples.

SCC Test Results

Initially, the SCC tests were conducted on indented samples. The test conditions were determined from the results of immersion tests. The results indicate that no stress corrosion cracks have occurred near indentation in any of the environments tested. Even though some pits were formed inside the indentation, no cracks have been propagated from the pits. The maximum duration of immersion in the active environments was 8 days. In a parallel study by Zaheer [15], Alloy 800 also did not show any stress corrosion cracks in

55

IMMERSION TESTS ON CHEMICALLY POLISHED SAMPLES

Sample #	Concentration	Duration hours	Observations
CP1	0.04M FeCl ₃	24	General corrosion and pitting attack on both surfaces, grain etching, some blisters are visible
CP2	0.03M CuCl ₂	24	The top face appears as polished with irregular shaped pits, the center of the bottom has general attack with grain etching and slight crevice attack, remaining surface is same as polished
CP3	0.044M (NH4)2S2O8	24	Some of the top and bottom surface has general attack and pitting and the remaining surface is same as polished surface, some black stains on both surfaces
CP4	0.02M FeCl3	48	Light grain etching and slight general attack on top, severe general attack and dark etching with some blisters on bottom
CP5	0.006M CuCl ₂	48	No general attack has occurred on either surfaces, many deep pits are observed on both faces, no grain etching, some blisters are visible
CP6	0.022M (NH4) ₂ S ₂ O ₈	48	Slight general attack and light grain et etching on top, severe general and pitting attack and dark etching on bottom

Figure 32. The Chemically polished surface of Alloy 200 at 95 C for 60 seconds shows many big and small size pits (180X)

Figure 33. The corrosion attack of Chemically polished Alloy 200 in 0.04M Ferric chloride solution for 24 hours shows Pitting attack leading to General corrosion (180X)



Figure 34. The Pitting attack of Chemically polished Alloy 200 in 0.03M Cupric chloride solution for 24 hours shows Pitting leading to General attack (180X)

Figure 35. The Pitting attack of Chemically polished Alloy 200 in 0.044M Ammonium persulfate solution for 24 hours shows many small size pits leading to General attack (180X)



Figure 36. The Pitting attack of Chemically polished Alloy 200 in 0.02M Ferric chloride solution for 48 hours shows many small size pits (180X)

Figure 37. The Pitting attack of Chemically polished Alloy 200 in 0.006M Cupric chloride solution for 48 hours shows few small size pits (180X)





Figure 38. The Pitting attack of Chemically polished Alloy 200 in 0.022M Ammonium persulfate solution for 48 hours shows pitting leading to General attack (180X) ferric chloride upto 10 days and in magnesium chloride at 180 F upto 30 days of immersion. But Markey [47] reported cracking in stainless steels by using this technique.

The SCC tests by slow strain rate technique were carried out in three environments, ferric chloride, cupric chloride, and ammonium persulfate. All the test specimens received the same heat treatment and the grain size is approximately $35 \,\mu$ m. All the samples were examined under the SZM after the fracture. All the test samples showed a cup and cone fracture. The corrosion attack exhibited varied from general attack to slight pitting. The observations of SCC tests are recorded in Table IX. The observations of test samples in each environment are discussed below:

SCC Tests in Ferric chloride solutions

Four tests were conducted in this environment. For the first test, the test conditions were 0.4 M concentration, time 5x10⁵ seconds at a stroke range of 100%. General corrosion has occurred all over the sample surface which is exposed to the active environment. Near fracture location, extensive gaping cracks have been observed on both the ends (Figures 39, 40, and 41). About 1/2 inch from the fracture surface, the pits are elongated parallel to loading direction and appeared as longitudinal cavities, on big end (Figures 42 and 43). No longitudinal inclusions were present in the gauge length surface. Some staining has been noted on fracture surfaces. Some general attack has been noticed in the vapor zone. No crevice attack has occurred at the o-ring.

For the second test, the solution concentration was 0.2M, at a time of 1×10^5 seconds and 100% range. General attack has occurred all over the gauge length. The observation of fracture surfaces showed many pits. No pitting was noticed in the vapor zone. Some small shallow cracks were observed near fracture zone. These cracks were blunted as they approach fracture zone. Some round and big deep pits were observed between shank and neck. Also, some pits have formed on fracture surface. No crevice attack occurred at the o-ring of environment chamber.

61

OBSERVATIONS IN SCC TESTS BY SST METHOD

Specimen #	Concentration	Ram speed seconds	Stroke Range %	Observations
1	0.4M FeCl3	5x10 ⁵	100	General attack all over the gauge length, some small pits between shank and neck, extensive gaping cracks near fracture zone, no crevice attack at o-ring
2	0.2M FeCl3	1x10 ⁵	100	General attack occurred all over the surface, many pits on fracture surfaces, some shallow blunt cracks near fracture zone, no crevice attack at o-ring
3	0.12M FeCl ₃	5x10 ⁵	20	The general attack is less severe than specimens 1 and 2, some elongated pits in gauge length, some shallow blunted cracks near fracture location, no crevice attack
4	0.02M FeCl3	5x10 ⁵	20	Some small pits and less general attack, and some gaping cracks near fracture end
5	0.03M CuCl ₂	5x10 ⁵	20	Crevice attack at o-ring on long end and the rest of the surface is unaffected, no appreciable amount of cracking near fracture end, small pits on small end
6	0.06M CuCl ₂	5x10 ⁵	20	Severe crevice attack than specimen #6, the gaping cracks at fracture are minimum, and no general attack on the rest of the surface

Specimen #	Concentration	Ram Speed seconds	Stroke Range %	Observations
7	0.022M (NH ₄) ₂ S ₂ O	5x10 ⁵	20	Some crevice attack at o- ring and some small size pits on the gauge length, no appreciable amount of cracking
8	0.04M (NH ₄) ₂ S ₂ O ₈	5x10 ⁵	20	The crevice attack is severe than specimen #7, gaping is minimal, some small size pits on the gauge length surface

. .

TABLE IX (Continued)

Figure 39. The side view of the fracture zone in 0.4M Ferric chloride solution. Extensive gaping cracks are seen in the vicinity of the fracture (30X)

Figure 40. The test details of the Figure 39 showing severe General attack and extensive gaping cracks (500X)





Figure 41. The test details of the Figure 40 at higher magnification (2000X)

Figure 42. The test details of Figure 39. The surface away from the fracture vicinity, showing General attack and elongated pits in the form of longitudinal cavities. The cracking is minimal (500X)

n n ru S N



For the third test, the concentration of solution was reduced to 0.12M and a time rate of 5×10^5 seconds at 20% range. This time and stroke range was used for all the subsequent tests in different environments. No elongated pits were observed on sample surface. Some general corrosion and small pits are visible. Some transgranular cracks have been observed near fracture location on both ends (Figures 44, 45, and 46). This cracking is less extensive than in specimen #1, and 2. These cracks tend to be blunted near fracture zone. Figures 47, and 48 show elongated pits away from the fracture. No crevice corrosion has been observed. In the vapor zone, some small pits were noticed.

In the fourth test, the concentration was 0.02M and the other conditions are same as mentioned above. The observations showed that little cracking has occurred near fracture location (Figures 49, 50, and 51). Both ends have etching near shoulders. Some small pits are seen away from the fracture (Figure 52). In the vapor zone, the surface became dull and has some pitting attack. The extent of corrosion attack was less severe than other specimens in ferric chloride solutions.

In a summary, all the SCC tests in ferric chloride solutions showed gaping cracks near fracture zone. The extent of cracking was severe at higher strain rates and higher concentrations of the solution. No crevice attack has been observed in all the tests. The extent of corrosion attack is varied from severe general attack to pitting. Also, some pits were observed on the fracture surfaces.

SCC Tests in Cupric chloride solutions

Two tests were conducted in this environment. For the first test, the concentration was 0.03M and the other conditions were same as mentioned before. Some crevice attack has been observed on big end at the o-ring on shoulder. The rest of the surface in gauge length was unaffected. This is due to the fact that the crevice portion acted as anode and corroded, and the the surface in gauge length is cathodically protected. This is also the reason for not observing any appreciable amount of cracking near fracture location. On the

66

Figure 43. The test details of the Figure 42 at higher magnification (2000X)

Figure 44. The side view of the fracture zone in 0.12M Ferric chloride solution. The transverse cracking with gaping is observed in the vicinity of fracture. The cracking is less extensive compared to Figure 39 (30X)





Figure 45. The test details of Figure 44 showing Pitting attack leading to General corrosion and gaping cracks (500X)

Figure 46. The test details of the Figure 45 at higher magnification (2000X)





Figure 47. The test details of the Figure 44. The surface away from the fracture vicinity showing some corrosion and longitudinal cracks. The corrosion attack is less severe than in Figure 42 (500X)

Figure 48. The test details of the Figure 47 at higher magnification (2000X)





Figure 49. The side view of the fracture zone in 0.02M ferric chloride solution. The surface shows many small pits and cracks. The gaping is less extensive than in Figures 39 and 44 (30X)

Figure 50. The test details of Figure 49 showing less corrosion attack and cracking compared to Figures 40 and 45 (500X)

•



Figure 51. The test details of figure 50 at higher magnification (2000X)

Figure 52. The test details of Figure 49. The surface away from the fracture vicinity showing some elongated pits. The corrosion attack is less severe than in Figures 42 and 47 (500X)





corroded, and the the surface in gauge length is cathodically protected. This is also the reason for not observing any appreciable amount of cracking near fracture location. On the small end, some light green deposit has occurred. Many small pits are visible away from the fracture surface on small end. Some shallow cracks are observed near fracture location (Figures 53, and 54). Some pitting attack was observed in the vapor zone.

The second test was conducted at 0.06M concentration, the extent of crevice attack was more severe than in the above mentioned specimen. The severe crevice attack has been noted on long end at the o-ring. Also, the cracking was minimal near fracture zone. Some longitudinal pits have been observed away from the fracture surface on small end. In the vapor zone the corrosion attack was much severe.

Ammonium persulfate solutions

Two tests were conducted in this environment. For the first test, the concentration was 0.022M, other test conditions remained same. Crevice attack has been observed at the o-ring on long end. The rest of the surface is cathodically protected and less affected. Also, no appreciable amount of cracking has occurred near fracture zone. On small end, near the neck portion, some pits were elongated. The surface is very lightly etched. Some transverse cracks have been observed at machining grooves. No general attack is observed. Some black colored stain marks were observed on long end. In the vapor zone, the surface is dull and has very few pits.

In the second test, the specimen geometry is different from all the other specimens. The gauge length was not waisted, but flat. The solution concentration was 0.04M. The crevice attack was much severe than in the specimen mentioned above. It should be noted that the extent of crevice attack in ammonium persulfate solutions is less severe than in cupric chloride solutions. This is the reason for having some pitting attack in the gauge length portion though it was acted as a cathode. The cracking was minimal near fracture location (Figures 55, 56, and 57). Figure 53. The side view of the fracture zone in 0.03M Cupric chloride solution. The cracking is minimal compared to tests in Ferric chloride solutions. Extensive deformation and many pits are visible (30X)

Figure 54. The test details of Figure 53 showing minimal cracking and corrosion attack (500X)





Figure 55. The side view of the fracture zone in 0.04M Ammonium persulfate solution. The cracking is minimal compared to tests in Ferric chloride solutions. Numerous pits are visible on the fracture surface (30X)

Figure 56 The test details of Figure 55 showing little cracking and corrosion attack compared to Figure 54 (500X)







Figure 57. The test details of the Figure 56 at higher magnification (2000X)

CHAPTER VI

DISCUSSION AND ANALYSIS

The objective of this thesis is to study pitting behavior and to explore any SCC of Alloy 200 at room temperature. The experimental work and results have been presented in the previous chapters. The pitting test results showed that all the environments tested have shown pitting attack at room temperature. Interestingly, the extent of attack is different in all the solutions. Cupric chloride solutions are the worst environment for the pitting corrosion resistance of Alloy 200. The other two environments, ammonium persulfate and ferric chloride have shown pitting attack in a decreasing order. Although all the solutions showed general attack at higher concentrations, the diluted cupric chloride solutions showed round and deep pits.

The corrosion rates of Alloy 200 in these three environments exceed 50 mpy at above 60 F which is unsatisfactory [48]. The concentrations of the standard test solutions are not mentioned in the reference. Also, these corrosion rates will increase with the increase of temperature. Therefore, Alloy 200 should be used only at lower concentrations to prevent any failure by corrosion.

The effect of solution concentration and time of immersion have a direct consequence on the pitting behavior of Alloy 200. This issue has been verified in the Fig.12, 13, 20, and 21. As a result, the number and/or size of the pits increase with the increase of solution concentration. Increasing the immersion time can also increase the pitting attack. However, it should be noted that there is a definite range of concentration and time period to observe the pitting in the specified environments. At higher

76
concentrations, samples will usually corrode within few hours of immersion, and pitting attack may change to general attack at longer durations.

The immersion test results indicate that Alloy 200 is susceptible to crevice corrosion in cupric chloride and ammonium persulfate solutions. Little crevice attack has been observed in ferric chloride solutions. It should be noted that crevice corrosion increases with solution concentration and bad surface finish. When the crevice attack is severe on bottom, only a small number of pits were observed on top surface. This is due to the fact that the top surface acts as a cathode and bottom as an anode and consequently the bottom will be affected most.

During the experimentation, it is observed that in cupric chloride solutions, more green deposits formed on the sample bottom surface. This may also be one of the reasons for the crevice corrosion to occur on bottom. Some undercutting is also associated with the crevice attack. As the solution concentration is decreased, the crevice attack is also reduced proportionately. This is due to the fact that the tendency for the formation of deposits is less in case of dilute solutions. The crevice attack is more severe in cupric chloride solutions than in ammonium persulfate. Lu [13] has reported crevice corrosion of Alloy 400 in ammonium persulfate solutions. Zaheer [15] has demonstrated crevice attack of Alloy 800 in ferric chloride solutions and he attributed this behavior to the amount of silicon content in Alloy 800. Zaheer reported that tendency towards crevice attack is higher in Alloy 800 as compared to Alloy 400 and Alloy 600. The maximum silicon content in Alloy 800 it is 0.35 by wt%, in Alloy 600 it is 0.5% where as in Alloy 800 it is 1.0%. Surface of samples should be free of scratches to avoid crevice corrosion.

The immersion tests in ammonium hydroxide and hydrofluoric acid have shown slight pitting attack. since the corrosion rates of Alloy 200 in these environments is comparatively less (20-50 mpy), the samples showed less attack. Also, these are not oxidizing acid salts. Everhart and Deardorff have demonstrated the effect of addition of oxidizing salts to hydrofluoric acid to increase the pitting attack of Alloy 400.

Some experiments have been conducted to verify the effect of surface condition on pitting behavior of Alloy 200. The results of pitting tests show that pit initiation is favored by inclusions, scratch marks, and dents on the surface. The scratches on the surface can be deleterious only if there is any residual stress present in it. However, it is often difficult to predict and to measure the magnitude and direction of these stresses. It was reported that there is no relation between pitting and the number of non metallic inclusions in case of stainless steels [20]. In case of Alloy 800, it was reported that titanium nitride inclusions act as favorable pit initiation sites [15]. The chemically polished samples showed many inclusions on the surface. But the pitting is not always initiated at these inclusions.

Previous studies on stainless steels indicated that surface depressions such as cracks, and striations cause pitting by serving as minute reservoirs for the accumulation and stagnation of corrosive salt solutions [20]. This would result in local concentration cell. The effect of polishing has been investigated in this thesis. The chemical polishing seemed to be more detrimental to the pitting corrosion resistance. These samples showed many pit initiation sites, pits and blisters. The subsequent immersion tests showed severe corrosion attack compared to mechanically polished samples. However, the pits initiated during chemical polishing did not grow in the subsequent immersion tests. Choday [43] made similar observations with Alloy 400.

These results are consistent with the findings by Streicher [20]. His studies on effect of polishing on stainless steels indicate that resistance to pit initiation increased with the degree of mechanical polishing. Also, the reason for the preferential attack of grain boundaries can be explained. During mechanical polishing, a layer of highly deformed metal will be produced on the surface, which probably covers the grain boundaries. In case of electrolytic or chemical polishing, metal will be removed selectively from the surface without the formation of a flowed metal layer to obscure grain boundaries. The formation of blisters during chemical polishing is probably due to the bubbling action and

entrapment of bubbles beneath the oxide films. The optimum test conditions such as composition, time and temperature may reduce this effect.

The pits observed during the immersion tests have various sizes and shapes. A visual examination of the metal surface showed round, elongated, or irregular shaped pits. In many cases, the pits on the top surface have regular shapes and on the bottom, irregular shaped pits are observed. The pit shape and size is likely to be dependent on the concentration of the solution. At higher concentrations, a small number of big size pits are observed on top and on the bottom irregular shaped pits are associated with some undercutting. It is often necessary to take a cross section of the pit to see its actual shape and to determine its true depth. Several variations in the cross-sectioned shape of pits are shown in Figure 58. A more detailed examination would include the measurement of maximum pit depth, average pit depth, and pit density [44, 45].

Some observations on morphology of pits revealed that the interior of the pit is consisted of shiny, and crystalline facets. In cupric chloride solutions, the interior of the pit is covered by green deposits in some cases. The size of the facets may vary along the depth in a regular fashion. The facets near the surfaces are tend to be finer and the size increases with the depth of pit. Some pits are associated with undercutting.

The distribution of pitting has been studied by numerous investigators using statistical techniques [45]. These experiments demonstrated that corrosion pits are not mutually independent events, and that pits interact with one another. This interaction is believed to be caused by the cathodic protection of the metal surface immediately adjacent to a pit site. In the present study, it was observed that most of the pits on top surface were distributed all over the surface and on the bottom they were distributed in the center. In some samples, lot of scratches were present near edges not at the center of surface. In a summary, pits were distributed in a different fashion on top and bottom surfaces, they were distributed more uniformly on top and randomly on bottom.

The SCC tests on indented samples showed no cracks, even though some deep pits



Figure 58. Various Configurations of Pits (From ASTM⁴⁴) were observed inside the indentation. The tests were conducted up to 8 days of immersion. Further experimentation at longer durations should have been carried out. This technique has shown successful results in case of austenitic stainless steels. The indentation operation sets up residual tensile stresses in and around the indentation. Although the magnitude of these residual stresses has not been quantitatively determined, the stresses vary from very low elastic stresses at the edge of indentation to high plastic stresses in the indentation.

The SST tests showed some transverse cracks which were wide open near the fracture location. The initial tests were conducted at comparatively concentrated solutions. All the specimens showed severe general attack and less pitting attack. As mentioned earlier, the SCC will be favored by localized attack, and cracks initiate from the pits. The subsequent tests using diluted solutions showed less general attack and well defined pits in the gauge length surface. In some samples, the elongated pits were observed away from the fracture location in the form of longitudinal cavities. All specimens showed a cup and cone type of failure. The extensive amount of plastic deformation has occurred in all the samples. Future tests could be conducted at lower strain rates to enhance the propagation of TG cracks on the entire cross-section of the specimen.

The solutions which showed crevice attack in immersion tests also showed the crevice attack in SCC tests on the shank portion at the o-ring. The o-ring used at the bottom of the environment chamber acted as a crevice former and caused crevice attack. It was already mentioned that crevice attack is more severe in cupric chloride solutions. This can be explained as, the cupric chloride solutions have the tendency to form deposits during immersion tests. These deposits together with crevice former, which is the o-ring in SCC tests, have provided more favorable conditions for stagnant conditions of the solution and caused severe attack. Because the crevice portion acts as an anode, the rest of the surface in the gauge length is cathodically protected. Hence, there is a less corrosion attack on gauge length in cupric chloride solution and minimal SCC.

In case of ferric chloride solutions, no deposits formed. This is the reason for not observing crevice attack in ferric chloride solutions during pitting as well as SCC tests. Hence, the corrosion attack is severe along the gauge length of tensile specimens. The ammonium persulfate solutions also provide favorable conditions for crevice corrosion. Similar observations have been reported by Zaheer [15] for Alloy 800.

There is a correlation between the pitting and the SCC results of Alloy 200. All the solutions used for SCC tests showed pitting during immersion tests as well as SCC tests. The observations of fracture surfaces showed many pits on the grains which were visible due to intergranular attack. Also in the gauge length, some elongated pits were observed away from the fracture location. The fracture might have started at this location. It can be expected that when optimum grain size and strain rates exist, more embrittlement may occur in Alloy 200 in these environments.

Comparison of Alloy 200 with other Nickel-base alloys

In this section, the experimental work and results on Alloy 400, Alloy 600, and Alloy 800 will be compared with Alloy 200.

Comparing with Alloy 200, Alloy 400 showed pitting attack in a wide range of environments. Even in 0.001M Ferric chloride and Ammonium persulfate solutions Alloy 400 has shown considerable pitting attack. Under these test conditions, Alloy 200 is hardly shown any pitting attack. Alloy 400 is also subjected to crevice attack in diluted Ammonium persulfate solutions. Both the alloys developed some pits and blisters during chemical polishing. Also, Alloy 400 showed embrittlement in a wide range of environments. For example, even in 0.005M Ammonium persulfate solution, an extensive amount of cracking has been reported for Alloy 400. In the same environments, Alloy 200 did not show appreciable amount of cracking. This may lead to a conclusion that Alloy 400 is more susceptible to pitting and SCC compared to Alloy 200 at room temperature.

Comparing with Alloy 200, the pitting and SCC susceptibility of Alloy 600 is higher in ferric chloride solutions. For example, Alloy 600 showed many small pits in 0.01M Ferric chloride solution within 10 hours of immersion. Both the alloys have shown an increase in pitting attack with solution concentration and time of immersion. Alloy 600 has also shown increasing pitting attack with temperature up to a certain limit. Because of the transpassive behavior, the corrosion resistance of Alloy 600 will be more at specific temperatures and concentrations [14]. The sensitization treatment considerably increased the pitting attack of Alloy 600. The carbide forming elements such as chromium are not present in Alloy 200. Hence, chromium carbide precipitation at grain boundaries will not occur at higher temperatures. Alloy 600 has shown crevice attack in SCC tests. Alloy 600 showed tremendous amount of embrittlement in 0.1M Ferric chloride solution. The sensitized alloy showed two kinds of microstructures, which are IG cracking on shoulders and microvoids in the neck region. Where as Alloy 200 has shown slight cracking under these conditions. Based on these discussions, it can be concluded that Alloy 600 is more susceptible to pitting and SCC in Ferric chloride solutions at room temperature compared to Alloy 200.

The immersion tests on Alloy 800 demonstrated that pitting attack readily occurs in Ferric chloride solutions. But Alloy 800 did not show appreciable amount of pitting attack in 0.6M Cupric chloride and 0.45M Ammonium persulfate solutions. Alloy 200 has shown significant amount of attack in these environments. However, the condition of the alloy is very important in assessing the pitting behavior of Alloy 800. It was reported that sensitized alloy has greater inclination towards pitting. For example, the unsensitized alloy showed only 3 pits in 0.4M Ferric chloride solution, where as the sensitized alloy showed more than 100 pits under the test conditions. The Alloy 200 is not affected by sensitization treatment. Alloy 800 has shown marked crevice attack in Ferric chloride solutions during immersion tests as well as Slow Strain Rate tests. But Alloy 200 did not show this attack in Ferric chloride solutions. However, it should be noticed that the concentrations of

solutions are different in each case. Alloy 800 was tested at fairly higher concentrations than Alloy 200. Both the alloys have demonstrated the similar observations regarding the dependence of pitting behavior on test conditions. Alloy 800 and Alloy 200 did not show any Stress corrosion cracks on indented specimens. No embrittlement was reported for Alloy 800 in Ferric chloride solutions during SST but got pronounced crevice attack same as that for Alloy 200 in cupric chloride. But some embrittlement has been reported in corrosion fatigue tests. Under the similar test conditions, Alloy 200 has showed some transverse cracking with gaping. Based on these comparisons it can be concluded that the Alloy 200 is more susceptible to pitting and SCC compared to Alloy 800.

The following inference can be drawn after comparing the results of Alloy 200 with other alloys discussed above.

(i) The alloys can be ranked with respect to their susceptibility to SCC in chloride solutions at room temperature, in a decreasing order as Alloy 400, Alloy 600, Alloy 200, and Alloy 800.

(ii) No SCC has occurred on indented samples on Alloy 200 and Alloy 800. The sensitization heat treatment has considerable effect on pitting and SCC behavior of Alloy 600 and 800.

(iii) Alloy 200 and Alloy 400 are susceptible to crevice attack in ammonium persulfate solutions and Alloy 800 in ferric chloride solutions.

(iv) The chemical polishing has the same effect on both Alloy 200 and Alloy 400. In both cases some pits were initiated after polishing and they did not grow considerably in subsequent immersion tests.

It should be noted that there is a correlation between pitting and SCC behavior for alloy 200 at room temperature. The solutions which showed pitting corrosion during immersion tests also showed SCC in SST.

CHAPTER VII

CONCLUSIONS

 Alloy 200 can be subjected to Pitting corrosion in a wide variety of environments which include Ferric chloride, Cupric chloride, Ammonium persulfate, Aerated Ammonium hydroxide, and Hydrofluoric acid solutions. The Cupric chloride solutions showed more corrosion attack with adherent deposits and undercut pits than other solutions.

2. The extent of Pitting attack increases with solution concentration and time of immersion under certain test conditions. The solutions of higher concentrations can cause severe General corrosion.

3. Alloy 200 is prone to Crevice corrosion in Cupric chloride and Ammonium persulfate solutions. The immersion tests in these environments showed Crevice attack at the bottom of the sample. This attack is severe in Cupric chloride solutions aided by the formation of thick and adherent green deposits.

4. The top surface of the samples showed less Pitting attack when there is a Crevice corrosion attack at the bottom. This is due to the fact that the top surface is cathodically protected while the bottom surface is acted as an anode.

5. The inclusions are favorable sites for the pit initiation. The Chemical polishing induces some pits and blisters on the surface of sample. These pits do not grow during the subsequent immersion tests. Mechanical polishing offers a better surface finish, compared to Chemical polishing.

Stress Corrosion Cracking can be induced in Alloy 200 at room temperature.
The Slow Strain Rate tests in Ferric chloride gave extensive embrittlement. Cupric chloride, and Ammonium persulfate solutions showed very limited embrittlement.

7. The solutions which showed Crevice corrosion in immersion tests also caused Crevice attack at the 0-ring of environment chamber during Slow Strain Rate tests. Due to the formation of crevices, the transverse cracking and gaping is less severe in Cupric chloride and Ammonium persulfate solutions.

8. There is a correlation between Pitting and SCC for Alloy 200 at room temperature.

A SELECTED BIBLIOGRAPHY

- 1. NACE News, Materials Performance, Vol. 22, Feb. 1983, p. 57
- 2. Fontana, M. G., <u>Corrosion Engineering</u>, 3 rd Edition, McGraw-Hill Book Company, NY c. 1986.
- 3. Asphani, A. I., "Corrosion of Nickel-base Alloys," <u>Metals Hand Book</u>, Vol. 13, 9 th Edition, ASM International, Metals Park, Ohio, PP. 641-657.
- Price, C. E., and J. K. Good, "The Tensile Fracture Characteristics of Nickel, Monel and selected Super-Base alloys broken in Liquid Mercury," Journal of Engineering Materials and Technology, ASTM, Vol. 106, April 1984, pp. 184-190.
- Price, C. E., and J. K. Good, "The Fatigue behavior of Nickel, Monel, and selected Super Alloys, tested in Liquid Mercury and Air: A comparison," <u>Journal</u> of Engineering Materials and Technology, ASTM, Vol. 106, April 1984, pp 178-183.
- Park, J. R., and Z. Szklarska Smialowska, "Pitting Corrosion of Inconel 600 in High Temperature water containing CuCl₂," <u>Corrosion - NACE</u>, Vol. 41, No. 11, 1985, pp. 665-675.
- Szklarska Smialowska, Z., D. Grimes, and J. Park, "The Kinetics of Pit growth on Alloy 600 in Chloride solutions at High Temperatures," <u>Corrosion -</u> <u>NACE</u>, Vol. 27, No.8, 1987, pp. 859-867.
- Price, C. E., and R. S. Fredell, "A Comparative study of the Embrittlement of Monel 400 at Room Temperature by Hydrogen and Mercury," <u>Metallurgical</u> <u>Transactions A</u>, Vol. 17A, May 1986, pp. 889-898.
- 9. Price, C. E., and L. B. Traylor, "Fractography of Hydrogen and Mercury Embrittlement in Nickel 200," <u>Corrosion - NACE</u>, Vol. 43, No. 4, April 1987, pp. 229-238.
- Price, C. E., and J. A. Morris, "The comparative Embrittlement of Example Nickel Alloys by Hydrogen and Mercury," <u>Journal of Materials for Energy</u> <u>systems</u>, ASM, Vol. 7, No. 3, Dec. 1985, pp. 246-255.
- 11. Everhart, L. G., "Stress Corrosion Cracking in Alloy 400 at Room Temperature," <u>Master's Thesis</u>, Oklahoma State University, Stillwater, May 1989.

- Everhart, L.G., and C. E. Price, "Stress Corrosion Cracking in Alloy 400 (UNS NO4400) at Room Temperature," <u>Corrosion Testing and Evaluation</u>, ASTM STP 1000, Philadelphia, 1990, pp 319-334.
- Lu Hung Sen., "Pitting and Stress Corrosion Cracking in Monel 400 at Room Temperature," <u>Master's Report</u>, Oklahoma State University, Stillwater, May 1990.
- 14. Hussen, I. A., "Corrosion Aspects of Alloy 600," <u>Master's Thesis</u>, Oklahoma State University, Stillwater, May 1991.
- 15. Zaheer, B. K., "An Investigation of Corrosion Behavior of Alloy 800," <u>Master's</u> <u>Thesis</u>, Oklahoma State University, Stillwater, May 1991.
- Uhlig, H. H., "New Perspectives in the Stress Corrosion Problem," <u>Physical</u> <u>Metallurgy of Stress Corrosion Fracture</u>, Metallurgical Society Conferences, Inter Science Publishers, N. Y., 1959 pp. 1-16.
- Graf, L., "Stress Corrosion Cracking in Homogeneous Alloys," <u>Stress Corrosion</u> <u>Cracking and Embrittlement</u>, W. D. Robertson, Editor, John Wiley & Sons, Inc., N. Y, 1956, pp. 48-60.
- 18. <u>Hand Book Of Huntington Alloys</u>, 4 th Edition., The International Nickel Company, Inc., Huntington, West Virginia, 1968.
- 19. Friend, W. Z., <u>Corrosion of Nickel and Nickel-Base Alloys</u>, John Wiley & Sons, Inc. 1980.
- Streicher, M. A., "Pitting Corrosion of 18 Cr 18 Ni Stainless Steels," Journal of Electrochemical Society, Vol. 103, No. 7, June 1956, pp. 375-390.
- Evans, U. R., "Stress Corrosion: Its Relation to other types of Corrosion," <u>Corrosion - NACE</u>, Vol. 7, July 1951, pp. 238-244.
- MacDougall, B., and M. J. Graham, "Formation and Breakdown of Passive Oxide Films on Nickel in Halide solutions," <u>Journal of Electrochemical Society</u>, Vol. 132, 1985, p. 2553.
- MacDougall, B., and D. F. Mitchell, "Incorporation of Chloride ion in Passive Oxide Films on Nickel," <u>Journal of Electrochemical Society</u>, Vol. 130, 1985, p 543.
- 24. Kaesche, H., Metallic Corrosion, 2 nd Edition., NACE, Texas, 1986.
- 25. Nishimura, R., "Pitting Corrosion of Nickel in Borate and Phosphate solutions," Corrosion - NACE, Vol. 43, No. 8, Aug. 1987, pp. 486-492.
- Greene, N. D., and M. G. Fontana, "A Critical Analysis of Pitting Corrosion," <u>Corrosion - NACE</u>, Vol. 15, Jan. 1959, pp. 41-47.
- Donald O. Sprowls., "Evaluation of Pitting Corrosion," <u>Metals Hand Book</u>, Vol. 13, 9 th Edition, ASM International, Metals Park, Ohio, pp. 231-233.

- 28. Scully, J. C., <u>The Fundamentals of Corrosion</u>, 2 nd Edition, Per Gamon Press, 1975.
- 29. Craig, B., "Environmentally Induced Cracking," <u>Metals Hand Book</u>, Vol. 13, 9 th Edition, ASM International, Metals Park, Ohio, pp. 145-189.
- Lynch, S. P., "Hydrogen Embrittlement and Liquid Metal Embrittlement in Nickel single Crystals," <u>Scripta Metallurgia</u>, Vol. 13, 1979, pp. 1051-1056.
- Kamdar, M. H., "Embrittlement by Liquid Metals," <u>Progress in Materials Science</u>, Vol. 15, No. 4, 1973, p.289.
- Gilman, J. J., "Stress Corrosion Cracking in Plastic Solids including the Role of Hydrogen," <u>Philosophical Magazine</u>, Vol. 26, 1972, pp. 801-812.
- Marcus O. Speidel., "Stress Corrosion Cracking of Aluminum Alloys," <u>Metallurgical Transactions</u>, Vol. 6A, 1975, pp. 631-651.
- Lynch, S. P., and P. Traveena, "Stress Corrosion Cracking and Liquid Metal Embrittlement in Pure Magnesium," <u>Corrosion - NACE</u>, Vol. 44, No. 2, Feb. 1988, pp. 113-124.
- Pickering, H. W., and P. R. Swann, "Electron Metallography of Chemical Attack upon some Alloys Susceptible to Stress Corrosion Cracking," <u>Corrosion -</u> <u>NACE</u>, Vol. 19, 1963, pp. 373t-389t.
- Mears, R. B., Brown, R. H., and E. H. Dix, JR., "A Generalized Theory of Stress Corrosion of Alloys," <u>Symposium on Stress Corrosion Cracking of</u> <u>Metals</u>, Philadelphia, A.S.T.M and A.I.M.E, 1944, pp. 323-339.
- 37. Logan, <u>The Stress Corrosion of Metals</u>, The Corrosion Monograph Series, John Wiley and Sons, Inc., 1966, pp. 178-192.
- Sieradzki, K., and R. C. Newman, "Brittle behavior of ductile metals during Stress corrosion cracking," <u>Philosophical Magazine A</u>, Vol. 51, NO. 1, 1985, pp. 95-132.
- Harwood, J. J., "The Phenomena and Mechanism of Stress Corrosion Cracking," <u>Stress Corrosion Cracking and Embrittlement</u>, W. D. Robertson, Editor, John Wiley & Sons, N. Y. 1956 pp. 1-20.
- Pugh, E. N., "On the Mechanisms of Stress Corrosion Cracking," <u>Environmental-Sensitive Mechanical Behavior</u>, Proceedings of the Metallurgical Society, Vol. 35, 1965, pp. 351-397.
- Copson, H. R., "Effect of Composition on Stress Corrosion Cracking of Some Alloys Containing Nickel," <u>Physical Metallurgy of Stress Corrosion Fracture</u>, Metallurgical Society Conferences, 1959, Inter Science Publishers, N. Y, pp. 247-269.
- Gary Winn Deardorff, "Pitting Studies on Nickel-Base Alloys at Room Temperature," <u>Master's Report</u>, Oklahoma State University, Stillwater, May 1989.

- Choday, V. Rao, "Pitting and Stress Corrosion Cracking Studies in Monel 400 and similar Alloys," <u>Master's Report</u>, Oklahoma State University, Stillwater, Dec. 1991.
- 44. ASTM G46 76 (Revised 1986), "Standard Practice for Examination and Evaluation of Pitting Corrosion," <u>Annual Book of ASTM Standards</u>, Philadelphia, 1987, pp. 268-275.
- ASTM G48 80, "Standard Test Method for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by the use of Ferric Chloride solutions," <u>Annual Book of ASTM Standards</u>, Philadelphia, 1987, pp. 284-287.
- 46. "Chemical Polishing," <u>Metallurgical Principles and Procedures</u>, Leco Corporation.
- 47. Markey Christopher, "The Effect of Solidification rate and Heat treatment on the Corrosion resistance of Ceramic shell Investment cast CF3M," Master's Report, Oklahoma State University, Stillwater, Aug. 1990.
- 48. Philip A. Schweitzer, <u>Corrosion Resistance Tables</u>, Marcel Dekker, Inc., N.Y.
- 49. Kain, R. M., "Evaluation of Crevice Corrosion," <u>Metals Hand Book</u>, Vol. 13, 9 th Edition, ASM International, Metals Park, Ohio, pp. 641-657.
- ASTM G78 83, "Standard Guide for Corrosion Testing of Iron-Base and Nickel-Base Stainless Alloys in Sea water and other Chloride containing aqueous Environments," <u>Annual Book of ASTM Standards</u>, Philadelphia, 1987, pp. 470-477.

APPENDIX

THEORIES OF PITTING CORROSION

The various theories and concepts used to explain the phenomenon of pitting attack are discussed in this section.

Imperfection Theory

In 1920, Seligman and Williams advanced this theory to explain the pitting corrosion of Aluminum. The authors stated that pitting would occur only if crevices or subsurface cavities were originally present in the metal. They also postulated that an autocatalytic reaction involving hydrogen peroxide occurred within pits. The importance of microscopic surface fissures as pit sites has been indicated by Wulff. Although surface cracks and imperfections can undoubtedly act as starting points for pitting attack, the electron microscopic studies indicate that pits probably can form independently of surface irregularities.

Peptization Theory

The Peptization theory of pitting attack was proposed by Evans in 1922 to explain the pitting tendencies of halide salts. Peptization refers to the transformation of a bulk precipitate to a colloid suspension. Halide ions are capable of peptizing many substances, including ferric oxide. Assuming the passivity of iron was due to a surface oxide layer, Evans proposed that chloride ions could destroy this layer at isolated points and allow attack to occur.

Penetration Theory

In 1927, Evans suggested that the specific pitting tendency of the chloride ion was due to its small diameter which permitted it to penetrate the protective oxide layer of iron. This theory was brought into prominence by the experiments of Britton and Evans in 1930. The authors applied a potential of two volts between two aluminum plates immersed in potassium dichromate solution containing additions of various salts and measured the resulting current flow. They concluded that the observed current flows were a direct measure of the abilities of the various anions to penetrate the protective oxide layer on aluminum surfaces.

The Penetration theory was effectively refuted by the work of Burwell and May in 1948. These investigators measured the permeability characteristics of oxide films isolated from aluminum surfaces. Diffusion, osmosis and electrical resistance measurements demonstrated that potassium chloride and potassium nitrate solutions penetrated the oxide films at almost identical rates. Burwell and May concluded that the exceptional corrosive action of chloride ion could not be the result of any special penetrating ability.

Adsorption Theory

The Adsorption theory of pitting became prominent during 1945-1947, notably due to work of Ershler, Hickling and Kabanov, Burstein and Frumkin. In general, the Adsorption theory postulates that pitting attack begins because chloride ions displace adsorbed oxygen or prevent it from adsorbing at isolated points on a metal surface. According to adsorption concept, the passive state is destroyed by the preferential adsorption of halide ions.

Acid Theory

All of the preceding theories are aimed primarily toward an explanation of the onset of pitting attack. With the exception of the Imperfection theory, none of them detail the

mechanism of pit growth. The acid theory of pitting was the first to describe a complete mechanism for pitting corrosion. The acid concept was formalized in 1947 by Hoar, who postulated that pitting corrosion is caused by pH changes that occur at anode areas. During corrosive attack in chloride solution, the chloride ions migrate to anode areas and increase the acidity at these regions. If the pH is low enough, the metal will dissolve as a soluble salt instead of precipitating as metal oxide or hydroxide. Apparently, this is an autocatalytic mechanism because increasing the acidity at anode regions increases the rate of anodic dissolution which in turn, causes a further increase in acidity.

Although the acid theory has been used usually in conjunction with the oxide film theory of passivity, this concept of passivity is not an essential assumption in the theory. Metallic passivity is destroyed in non-oxidizing, highly acidic environment containing halides. Thus, the acid theory is valid, independent of passivity mechanism.

Ion Exchange Theory

Piontelli advanced in 1950 the Ion exchange theory in an attempt to fundamentally explain the corrosion behaviors of the various anionic species. This theory is not a theory of pitting attack but a general concept which can be applied to pitting. Pointelli postulated that the influence of anions on electrochemical processes is primarily a result of their catalytic effect on electrode ionic exchange reactions; they affect electrode reactions without being consumed by them. According to the theory, the catalytic influence of anions is essentially determined by their polarizabilities or deformabilities. Highly polarizable anions, such as the halides, catalyze or accelerate electrochemical ion exchange processes; non-polarizable anions, such as perchlorate or sulfate, retard these processes.

Magnetic Theory

Studies of the pitting of iron and steel water led Ackerman to the conclusion that the localized attack was caused by magnetic poles on the metal surface. These magnetic poles

were believed to be induced in ferrite patches by the earth's magnetic field. Although Ackerman's concept of pitting corrosion seems rather dubious, it does suggest an interesting idea in regard to the pitting of non-magnetic ferrous alloys such as the austenitic stainless steels. Ferrous and ferric salts are highly paramagnetic and attracted strongly by magnetic fields. Hence the ferrous salt corrosion products during exposure to a pitting corrosive would be expected to accumulate at any magnetically permeable areas on an austenitic stainless steel surface and thus promoting pitting at these points. This may be a possible explanation of the lower pitting resistance of ferrite-containing stainless alloys.

VITA

RAJU S. KALIDINDI

Candidate for the Degree of

Master of Science

Thesis: PITTING AND STRESS CORROSION CRACKING IN ALLOY 200

Major Field: Mechanical Engineering

Biographical:

- Personal Data: Born in Srungavruksham, Andhra Pradesh, India, June 1, 1962, the son of Mr. and Mrs. Raju R. Kalidindi. Husband of Praveena Kalidindi and Father of Vamsi K. Kalidindi.
- Education: Graduated from Parishadh High school, Andhra Pradesh, India, in March 1977; received an Associate Degree in Mechanical Engineering from S.M.V.M. Polytechnic, India, in June 1980; received Bachelor of Engineering Degree in Mechanical Engineering from Bangalore University, India, in December 1984; received Master of Technology Degree in Industrial Metallurgy from Kakatiya University, India, in August 1987; completed requirements for the Master of Science Degree at Oklahoma State University in December 1991.
- Professional Experience: Teaching Assistant, Department of MAE, Oklahoma State University, January, 1990 to May, 1991; Assistant Engineer, Singareni Collieries Company Limited, India, January, 1988 to May, 1989; Engineer Trainee, Pressure Vessels Limited, India, August, 1987, to December, 1987; Internship, BHPV Limited, R&D division, India, November, 1986, to May, 1987; Summer job, Nagarjuna Steels Limited, India, June, 1986, to July, 1986.

Professional Affiliations: Student member of ASME.