CORROSION ASPECTS OF ALLOY 600

BY

IHSAN ALI HUSSEN

Bachelor of Science

in Mechanical Engineering

University of Baghdad

Baghdad, Iraq

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
May, 1991

CORROSION ASPECTS OF ALLOY 600

Thesis Approved:

Thesis Advisor

Dean of the Graduate College

ACKNOWLEDGMENTS

I would like to express my appreciation to those who have helped during this study. Special thanks to Dr. C. E. Price, my advisor for his instruction, encouragement, and advice throughout this study. Without his wisdom, this study would not possible. Thanks also to Dr. Good and Dr. Shiau for serving as committee members.

I would also like to thank the school of Mechanical and Aerospace Engineering at Oklahoma State University for their equipment and materials.

Finally, I would like to thank my government, my family and my friends each and every one for their support. I love you all.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure Page

Figure | Page

CHAPTER I

INTRODUCTION

Alloy 600 (UNS N06600) is a nickel base alloy, basically 76% Ni, 16% Cr, and 7% Fe (1,2,13,14). It is used in nuclear, chemical, aerospace, and other industries, because of its corrosion resistance. It has a corrosion rate of less than 0.01 mil/year, after 15 years of exposure to the atmosphere with no measurable loss of strength or ductility (1,14). However, Alloy 600 is susceptible to pitting corrosion in chloride solutions, such as ferric and cupric (13-15,19). Friend (13) said that a ferric chloride solution is frequently used to determine and measure the susceptibility of nickel-base alloys to chloride pitting. In this thesis, the effect of ferric chloride concentration on the pitting corrosion of Alloy 600 was studied. Also, the effect of three different temperatures and time on the pitting corrosion of Alloy 600 for each concentration was studied. Furthermore, the effect of a sensitized heat treatment was studied and compared with an unsensitized one to find out their effect on the pitting corrosion resistance of the alloy.

Since Alloy 600 has a tendency toward environmental assistant cracking (EAC), stress corrosion cracking (SCC) tests were conducted in ferric chloride solutions and liquid mercury to find out their effect. Again, the effect of a sensitized heat treatment was studied and compared with an unsensitized one to find out their effect on the SCC resistance of the alloy. Additionally, another study of hydrogen embrittlement (HE) and liquid metal embrittlement (LME) of Alloy 600 were taken into consideration for comparison to the SCC tests (20). Several studies of SCC tests have been conducted at high temperatures where Alloy 600 has relatively low SCC resistance (7,8,10,11,16). However, the SCC study of this thesis was conducted at room temperature like others which were conducted in different solutions (5).

Both SCC and pitting are caused by localized corrosion, but since SCC cracks could start at pits (11), a correlation between pitting corrosion and SCC could be explored as a guide for more details to SCC susceptibility. Furthermore, SCC tests in the same environments that cause pitting can be useful during the studies of SCC tests with the presence of stress in slow strain rate tests (SSTs).

Price and Good (20) conducted a fatigue study of Alloy 600 in liquid mercury. In this thesis, the effect of sensitized heat treatment was studied in liquid mercury too, then its results was compared with their results.

CHAPTER II

GENERAL CHARACTERISTICS OF Alloy 600

Composition

Alloy 600 is a nickel - chromium - iron alloy (1,13,14). The chemical compositions is in table I (14).

The high nickel content provides good corrosion resistance in environments such as hot caustic alkalis and high temperature halogen gases, except fluorine. The chromium content increases the strength, the resistance to an attack by sulfur compounds, and resistance to come acid solutions containing oxidizing salts, except chlorides (13). Iron does not increase nickel - base alloys corrosion resistance, but it improves resistance to sulfuric acid in concentrations above 50%. Iron also increases the solubility of carbon in nickel, which improves the corrosion resistance in carburizing environments at high temperatures (2).

Mechanical Properties

Alloy 600 is an FCC solid solution alloy with good formability (1,13,14). A range of tensile strengths, elongations, and hardness can be obtained by a cold work treatment (14). For example, in the annealed condition, a tensile strength of 172 - 345 MPa can be obtained, while in heavily cold - worked, a tensile strength of up to 1517 MPa can be obtained.

TABLE I

CHEMICAL COMPOSITION

Element	Weight per cent
Nickel (plus cobalt)	72.0 min.
Chromium	14 - 17
Iron	6 - 10
Carbon	0.15 max.
Manganese	1.0 max.
Sulfur	0.015 max.
Silicon	0.5 max.
Copper	0.5 max.

Sensitization

The heat treatment of Alloy 600 to the range of 540 - 760 C is called the sensitization range (3,14). Alloy 600 and other nickel base alloys could become susceptible to intergranular corrosion in certain severe corrosive environments such as oxidizing chlorides when the alloy is in heat sensitized condition. This means a precipitate of chromium carbides forms at the grain boundaries, when heated to this sensitization range (3).

Applications

Alloy 600 is used in different fields with temperatures from cryogenic to above 1095 C.

In the chemical industry, it is used in condensers, evaporators, heaters, stills, and bubble towers. In the heat - treating industry, its applications include mufflers, retorts, roller hearths, and furnace components.

In the aerospace industry, it is used for engine and airframe components such as exhaust liners, lockwire, and turbine seals (14).

Alloy 600 is used in nuclear reactors because of its excellent corrosion resistance to high-purity water, and the absence of chloride - ion SCC in reactor water systems, unless the alloy is in sensitized condition (1,2,14,20).

CHAPTER III

GENERAL CORROSION BEHAVIOR

Alloy 600 has a high nickel - chromium composition which gives the alloy high corrosion resistance to many organic and inorganic compounds (1,3,13,14,18).

However, the corrosion behavior of Alloy 600 depends strongly on the environment that this alloy experience.

The alloy has very good corrosion resistance in rural and marine atmospheres, but not very good in an industrial atmosphere, because it has sulfur in it (2,14,18).

Also, Alloy 600 has a very good resistance in fresh water and salt water spray, but pitting may occur in stagnant sea water. Furthermore, this alloy has excellent corrosion resistance in primary and secondary waters in nuclear reactors. Generally, Alloy 600 is immune in all mixtures of steam, air, and carbon dioxide (14,18).

Alloy 600 has fair resistance to sulfuric acid at room temperature, but poor resistance to sulfuric acid at boiling temperature (14).

It has good resistance to phosphoric acid at room temperature at all concentrations, but poor resistance at the boiling temperature (14,18).

Generally, this alloy has poor resistance to nitric acid

(14,18), and SCC occurred in 25% boiling nitric acid (8), but it has good resistance to organic acids and alkalis (2,14,18).

However, this alloy has poor resistance in both hydrochloric and hydrofluoric acids, especially at high temperatures (14).

It is also known that Alloy 600 is unaffected in dry chlorine or dry hydrogen chloride at room temperature (14). It is also unaffected in acid salts such as magnesium chloride at all temperatures (18), but wet chlorine and wet hydrogen chloride are corrosive to Alloy 600, especially at high temperatures (14).

Pitting Corrosion

Alloy 600, like stainless steel, is susceptible to pitting corrosion, especially in chloride environments (12,13,15,19,22). Ferric chloride is the solution most frequently used to study the susceptibility of nickel base alloys to chloride pitting (13).

Pitting is a form of localized corrosion which attacks specific parts of the alloy, eventually forming holes in these parts (2,12).

Generally, the number and size of pits increases with increasing concentration of chloride solution as well as with increasing temperature. For example, there was more pitting corrosion in 0.1 M cupric chloride specimens than 0.01 M specimens (19). However, at any concentration there will be a specific temperature where pitting starts where below this temperature there will be no attack; this temperature is called the critical pitting temperature (2). Alloy 600 shows good pitting corrosion resistance at high temperature if the surface of the alloy is clean (2,19). In other words, cleaning plays an important role in improving the pitting resistance. For example, impurity elements in Alloy 600, such as sulfur, play an important role in increasing the pitting of this alloy where these impurities could be the starting points of pitting (19).

It has been found that the corrosion products in these pits were enriched in chromium, with small amount of copper, sulfur, and chlorine. However, the corrosion products that cover the pits had additional enrichment of iron (19,22).

It has been found that active pit development consists of three stages; initiation, propagation and repassivation. When the pit repassivates, it will be no longer active unless the solution in this pit changes, then it might reactivate. Also, the larger the solution volume, the more pit initiation, but less depth, because of large anodic ions such as Cu^{2+} and less cathodic area (9).

Alloy 600 is a transpassive alloy which means it could have more pitting resistance at specific range of high temperatures than low temperatures, because of the protected oxide film that forms at those high temperatures (2,19,22). For example, examining specimens of Alloy 600 in 0.01 M and 0.1 M $CuCl_2$ at 60 C and 280 C showed there was more corrosion resistance at 280 C than 60 C in both concentrations (19).

Alloy 600 showed more pitting corrosion at longer times. For example, after 8 weeks of exposure in 0.1 M tetrathionate solution, it was found that the pits became bigger than the pits formed after 2 weeks (6).

Pitting Mechanism

The pitting starts with a breakdown of passivity at some points on the alloy surface which are less corrosion resistant, because of the presence of inclusions or any defect on the metal surface such as scratches or holes. After the breakdown, an electrolytic cell will be formed. The anode of this cell is the smallest part which is the active (breakdown) metal and the cathode is largest part which is the rest area of passive metal. The larger the cathode the fewer, deeper, and more active the pits, but if the size of the cathode is small, the pits will be more but of less size and depth. Because of the large potential difference between the active and passive areas, a flow of current will start from the anode causing a speedy corrosion (pits) to this anode. Once the pits are produced, they might grow by a self sustaining, or an autocatalytic process. The corrosion process inside the pits create conditions stimulating and necessary for the continuing activity of the pits. The growth and development of the pits is controlled by the depolarization rate at the cathode areas. Ferric chloride is a more effective depolarizer than surrounding dissolved oxygen, which causes greater numbers of pits and more rapid penetration (2).

The anodic metal reaction at the lowest part of the pits ($M \text{ ----> } M^{n+} + ne$) is balanced by a cathodic reaction on the rest of the metal surface ($O_2 + 2H_2O + 4e \text{ ---->} 4OH^-$). Increasing the concentration of the metal ions (M^{n+}) within the pits will cause the migration of chloride ions (Cl^-) to these pits to keep neutrality. Both metal and chloride ions from (M^+Cl^-) which will be hydrolyzed by water to hydroxide and free acid ($M^+Cl^- + H_2O \text{ -----> } MOH + H^+Cl^-$). As a result, The pH values at the bottom of the pits will be lower than the pH values of bulk solution which remains neutral (2,12).

Stress Corrosion Cracking

Since the tendency of austenitic alloys to SCC decreases with increasing nickel content, Alloy 600, that has about 72% nickel, has very good chloride SCC resistance, especially at low and medium temperatures (14,18).

However, Alloy 600 is known to have SCC at high temperatures, in high strength caustic alkalis (10,13,14,17), ferric chloride solutions (13), and mercury (14,20).

Some SCC attack has been found in Alloy 600 at room temperatures (22 C) in the presence of sulfur, such as sodium thiosulfate, sodium tetrathionate, and ferric sulfate - sulfuric acid (4-6). In addition, the SCC attack has been reported to cause IG attack, if it is preceded by pitting attack in sulfur environments such as thiosulfate and tetrathionate (4,6). Mostly, this IG attack is caused by chromium depletion from the grain boundaries, because of heat treatment of Alloy 600 within the sensitized range (540 - 766 C) prior to the tests (4-6,13,14).

Generally, the susceptibility of Alloy 600 to SCC, especially IG attack could be reduced by heat treatment to 900 C for one hour or 788 C for four hours prior to use with minimum operating stress, because it gives a uniform microstructure and mechanical properties (3,13,14). Bandy and Rooyen (6) suggested another heat treatment in caustic environments.

Correlation Between Pitting and SCC

It has been found that samples immersed in 0.1 M NaCl at 250 C developed pits led to IG attack. Those pits penetrated deep inside and attacked the grain boundaries (15).

In SSTs, it was found that pitting preceded the IG attack under certain environments such as 10^{-5} M tetrathionate (4), 0.1 M terathionate (6), 1.0 M H_2SO_4 + 10 ppm K ScN (21).

All the above agreed that a sensitized heat treatment led to the IG attack (4,6,21).

Such an IG attack has been observed in pressurized water reactor (PWR) steam generators, particularly within sludge that accumulate on the lower tube sheet (15,22).

Hydrogen and Mercury Embrittlement

Price and Good (20) conducted some experiments on Alloy 600 concerning mercury (LME) and hydrogen (HE). The fractography of mercury was more brittle than hydrogen, but the crack initiation was easier in hydrogen, which created a larger deformation region than mercury. As a result of that, the fractography of mercury was an intergranular (IG) cracking, except for the samples at higher temperatures (1100 C) for 10 hours which created some transgranular (TG) cracking at the necked region. As a contrast, the fractography of hydrogen was more mixed of IG and TG cracking. The shoulder region showed an IG microstructure, while the necked region showed mixed IG and TG cracking. This TG microstructure suggests the ductile deformation of the sample.

Fatigue in Hydrogen and Mercury Environments

Price and Good (20) conducted a study on fatigue in both mercury and hydrogen environments. Both microstructures began with IG cracking and ended up with TG cracking and microvoids. The difference is that the fracture was more brittle in mercury than in hydrogen. For example, the mercury samples showed some IG and TG secondary cracks and tearing while in hydrogen samples there was none. Another difference is that hydrogen samples showed larger TG cracking zones than the ones of mercury, which suggests the ductile fracture.

CHAPTER IV

PROPOSED INVESTIGATION

In this thesis, the following aspects will be explored:

1. The effect of concentration, temperature, and time on the pitting corrosion resistance of Alloy 600 in different concentrations of ferric chloride.

2. The critical pitting temperature.

3. Pitting development.

4. The effect of sensitized and unsensitized heat treatment on pitting corrosion resistance.

5. The correlation between pitting and SCC.

6. The susceptibility of Alloy 600 to intergranular attack during pitting tests.

7. The fractography of SCC and fatigue tests in ferric chloride solutions and liquid mercury.

8. The effect of sensitized and unsensitized heat treatment on the fractography of SCC tests.

9. Comparison between SCC, LME, HE, and fatigue fractographies.

CHAPTER V

EXPERIMENTAL PROCEDURES

Pitting Tests

Sample Preparation

Round discs of 12.7 mm diameter were cut from a long bar of Alloy 600, 8-13 mm high. The top surface of each sample was sanded through a 600 grit finish then polished through 0.05 μm alumina. Finally, the samples were rinsed in water, flooded with methanol, and dried with blowing air.

Test procedure

The samples were tested in ferric chloride solutions of 0.01 M, 0.03 M, and 0.1 M concentrations for comparison. Each sample was suspended so that only one surface of the sample was immersed in the solution inside a beaker. The suspending procedure was chosen to ensure that crevice corrosion would not interfere with pitting corrosion.

The samples were tested at three different temperatures low (3 C), room (24 C), and elevated (58 C). The samples were immersed for 5, 10, 20 hours in all concentrations for comparison and evaluation. However, at high concentrations (0.1 M), the samples were tested for less time (1,2.5) hours for comparison and evaluation of the early stages of pitting, because of the severe pitting attack at longer times.

After each duration, the samples were cleaned up under methanol and water then dried under warm air blow. Then the samples were examined under the microscope and photos were taken for explanation.

Slow Strain Rate and Fatigue Tests

Sample Preparation

The specimens for the SCC tests were waisted with a 0.25 inches minimum diameter, that gradually increased to 0.5 inches at the shoulders at the end of each gage length. Each specimen was either heat treated to the sensitized or unsensitized condition. Sensitized specimens were heat treated to 1100 C for 10 hours then the temperature was reduced to 700 C, which is within the sensitized range (540 -760 C), for 12 hours then cooled slowly in the furnace. Unsensitized specimens were heat treated to 1100 C for 10 hours then quenched in water. After heat treatment, each specimen was sanded through a 600 grit to remove the oxide film on the gage length then polished through 0.05 μm alumina. Finally, they were water rinsed, methanol flooded, and warm air dried.

SCC and Fatigue Test Procedure

The SCC tests used the SST procedures on an MTS machine. The stroke control was set on 20% with 50% load and 100% strain. The ram displacement rate was set at 5.0 x 10^{+5} second for the tests. The SCC tests were conducted in 0.1 M ferric chloride solution and liquid mercury. The solutions were put around the gage length through a special container to ensure that only the gage length was immersed and to prevent the solution from escaping or spilling out. The machine was under stroke control until the specimen broke.

After the specimens broke, they were removed from the grip, sonic cleaned, water rinsed, methanol flooded, and blown air dried.

A coupon of approximately 0.5 inches length from the fracture surface was cut from each sample and took under a JEOL JSM - 35 Scanning Electron Microscope for examination.

CHAPTER VI

RESULTS

Pitting Results

The general observations of Alloy 600 in ferric chloride solutions are shown in table II.

Most of these results indicate the increase of pitting corrosion with the increase of ferric chloride concentration. For example, in examining the samples photos for 10 hours in room temperature (24 C), it was found that number and / or size of pits, with compare to each other in same magnification, is larger in 0.1 M concentration (figure 1) than 0.03 M (figure 2) and 0.01 M (figure 3) concentrations. Also, most of the results indicate that pitting corrosion increases with the increase of temperature. For example, in examining the samples photos of 0.1 M concentration for 5 hours, the size of pits, with compare to each other in same magnification, is larger at higher temperature (58 C) (figure 4) than the one in room temperature (figure 5) and the one at low temperature (3 C) (figure 6). However, it was not always the case with respect to the samples of 0.01 M concentration for 10 hours. Though the increase of temperature, the samples showed less number of pits with almost the same size (figures 7,3,8). That is because of the transpassive

TABLE II

PITTING TEST DATA

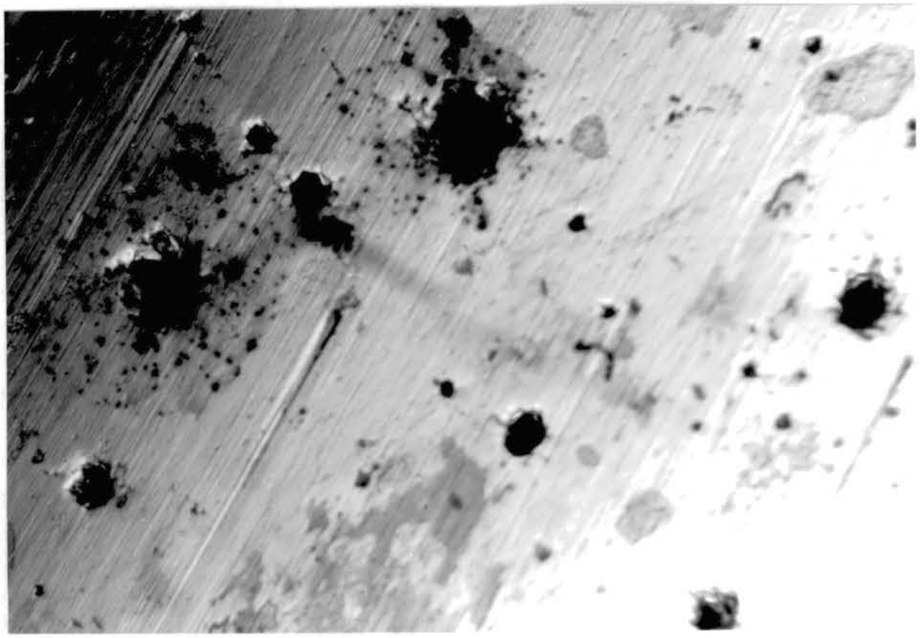
Concentration	Time	Temperature C	Observations
0.01 M	5 hrs	3	A
		24	A
		58	B
	10 hrs	3	B-D
		24	B
		58	B
	20 hrs	3	B-D
		24	D
		58	D
0.03 M	10 hrs	3	A-B
		24	B
	20 hrs	3	B
		24	B-C
0.1 M	1 hr	3	B
		24	B
		58	C
	2.5 hrs	3	B
		24	B
		58	C
	5 hrs	3	A-B
		24	B-C
		58	C
	10 hrs	3	B-D
		24	B-C
	20 hrs	3	B
		24	C

A: no pitting, B: small pits, C: large pits,

D: general pitting.

Figure 1. The Pitting Attack of Alloy 600 in 0.1 M Ferric Chloride Solution for 10 hrs at 24 C Shows Mixed of Small and Large Pits (200X)

Figure 2. The Pitting Attack of Alloy 600 in 0.03 M Ferric Chloride Solution for 10 hrs at 24 C Shows Small and Medium Pits (200X)



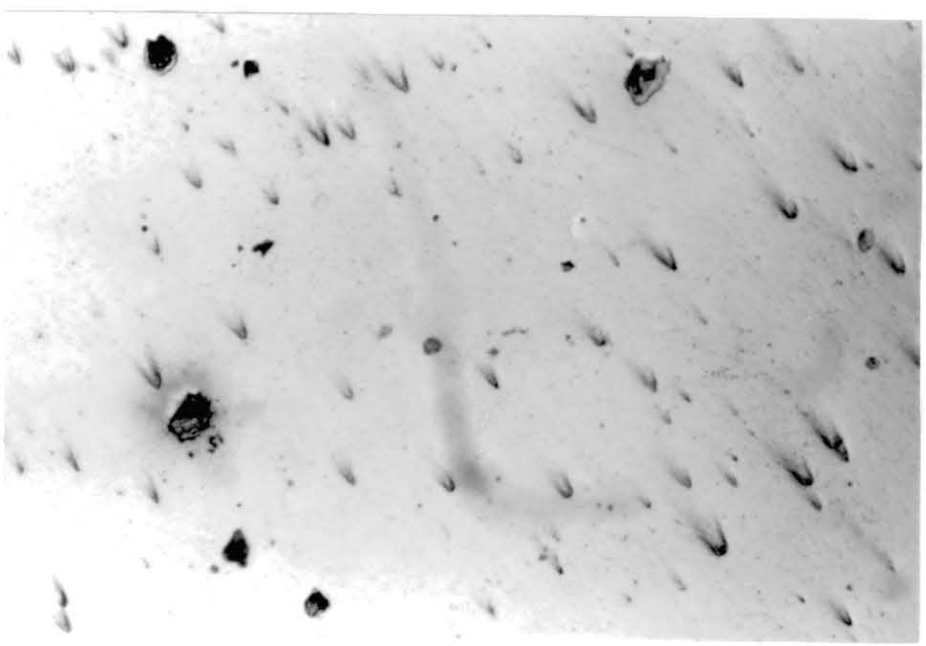
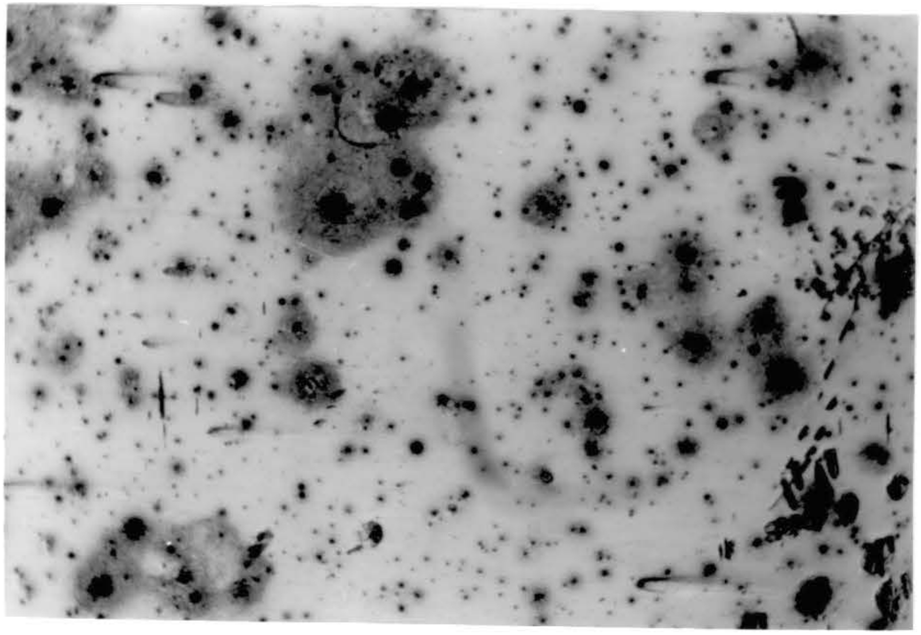


Figure 3. The Pitting Attack of Alloy 600 in 0.01 M Ferric Chloride Solution for 10 hrs at 24 C Shows Many Small Pits (200X)

Figure 4. The Pitting Attack of Alloy 600 in 0.1 M Ferric Chloride Solution for 5 hrs at 58 C Shows Large Pits and a Later Stage of Pitting Development (200X)



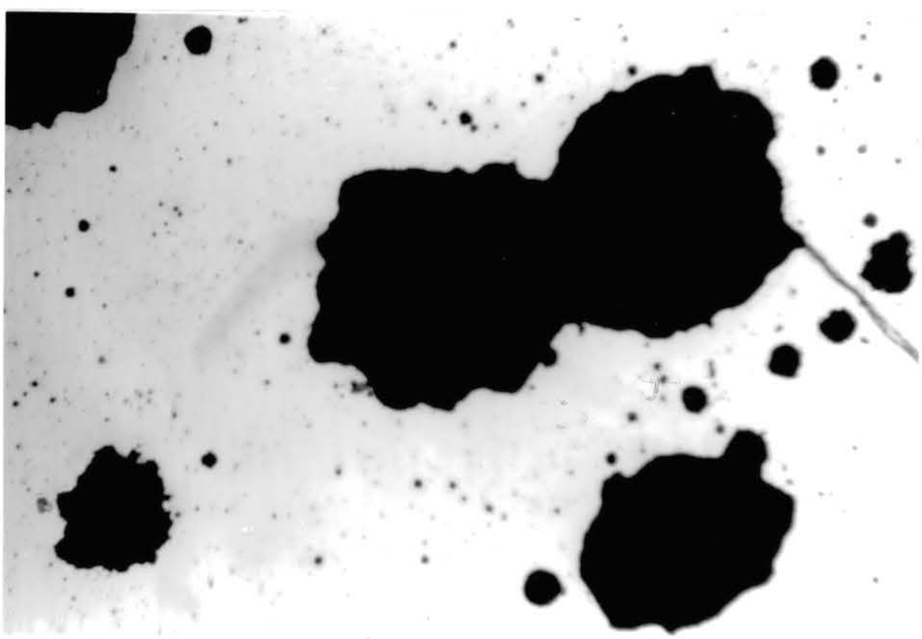
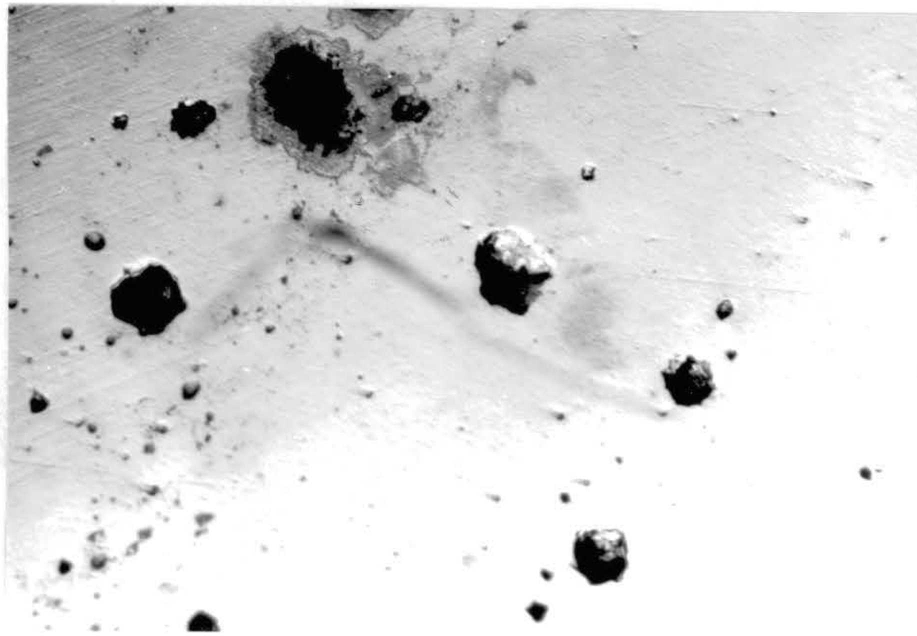


Figure 5. The Pitting Attack of Alloy 600 in 0.1 M Ferric Chloride Solution for 5 hrs at 24 C Shows Small and Medium Pits (200X)

Figure 6. The Pitting Attack of Alloy 600 in 0.1 M Ferric Chloride Solution for 5 hrs at 3 C Shows Small Pits and an Earlier Stage of Pitting Development (200X)



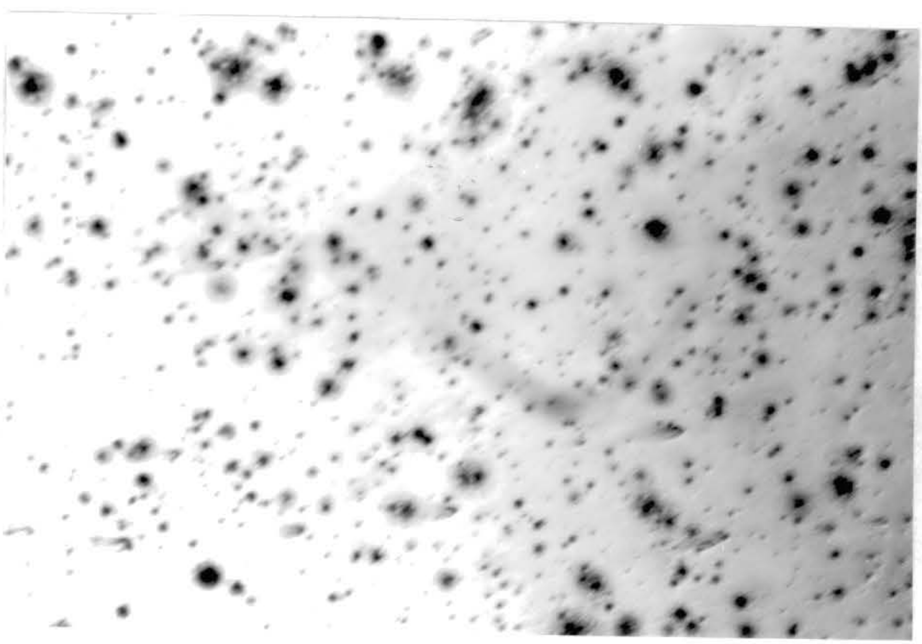
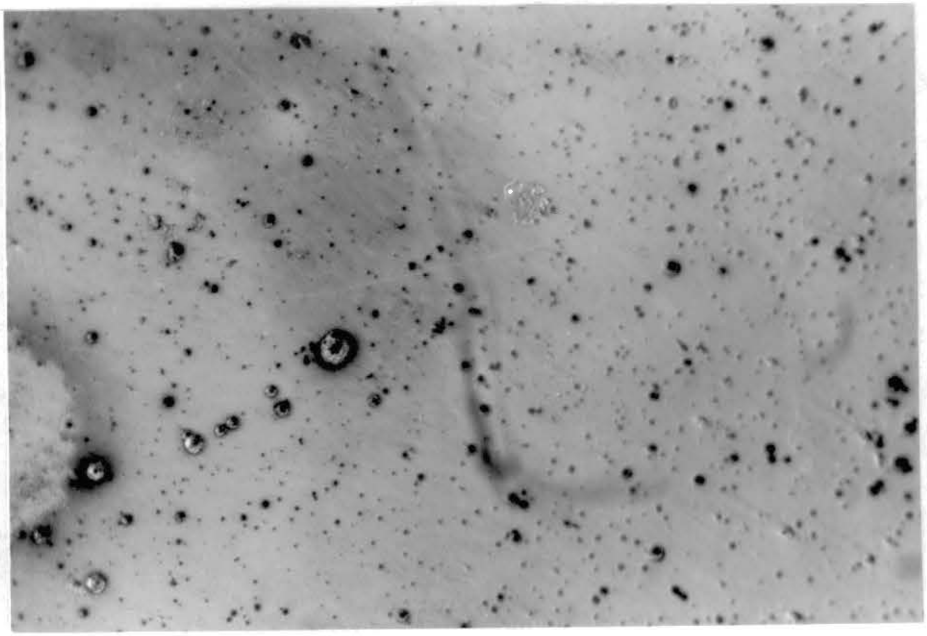
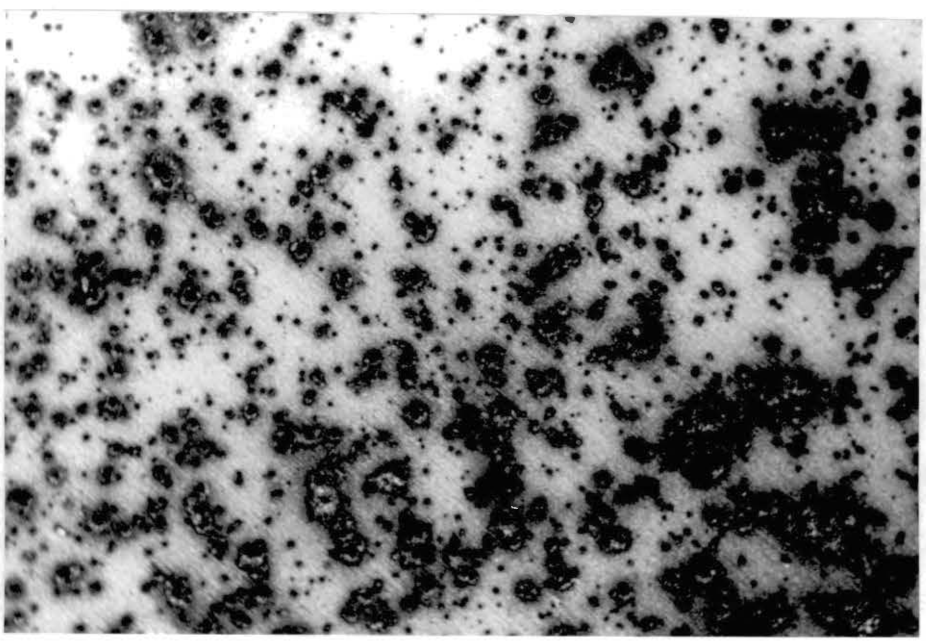


Figure 7. The Pitting Attack of Alloy 600 in 0.01 M Ferric Chloride Solution for 10 hrs at 58 C Shows Few Small Pits (200X)

Figure 8. The Pitting Attack of Alloy 600 in 0.01 M Ferric Chloride Solution for 10 hrs at 3 C Shows Many Small Pits and Close to a General Corrosion (200X)



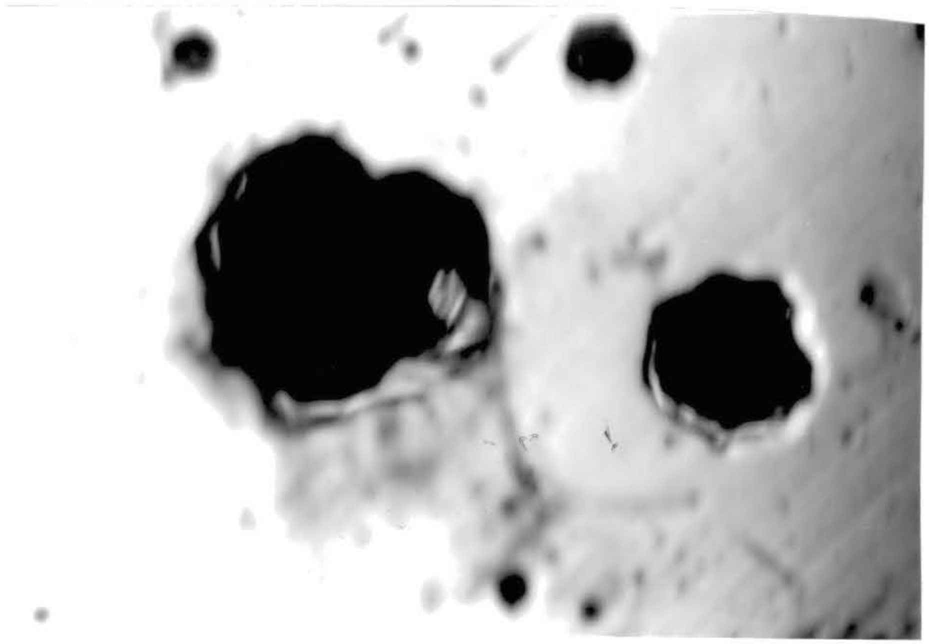


behavior of Alloy 600 which could lead to more corrosion resistance at specific high temperatures in specific concentrations as Park and Szklarska - Smialowska (19) got in their results. Most of the results also indicate that pitting corrosion increases with the increase of time. For example, in examining the samples photos of 0.1 M concentration at room temperature, the size of pits of 20 hours sample (figure 9) is larger than 10 hours sample (figure 1), 5 hours sample (figure 5), and 2.5 hours sample (figure 10). However the size of pits was not always the indication of increasing pitting corrosion with the increase of time. The exception was the samples of 0.01 M ferric chloride concentration. At longer times, the corrosion behavior changed from pitting corrosion to general or uniform corrosion at longer time which is more severe than pitting. For example, the 20 hours sample at high temperatures (58 C) showed general corrosion (figure 11), while the 10 hours sample showed pitting corrosion (figure 7).

These results can show the critical pitting temperature of Alloy 600 in three different concentrations of ferric chloride. Since the ASTM (5) test used 24 hours to find out the critical pitting temperature, the 20 hours sample will be used for this purpose. However, since the tests were conducted through different times, it became interesting to find out or expect the early stages of pitting. For 0.01 M concentration, the 20 hours sample at 3 C showed a severe pitting attack (figure 12). As a result of we can assume

Figure 9. The Pitting Attack of Alloy 600 in 0.1 M Ferric Chloride Solution for 20 hrs at 24 C Shows Large Pits and a Later Stage of Pitting Development (200X)

Figure 10. The Pitting Attack of Alloy 600 in 0.1 M Ferric Chloride Solution for 5 hrs at 58 C Shows Large Pits and a Later Stage of Pitting Development (200X)



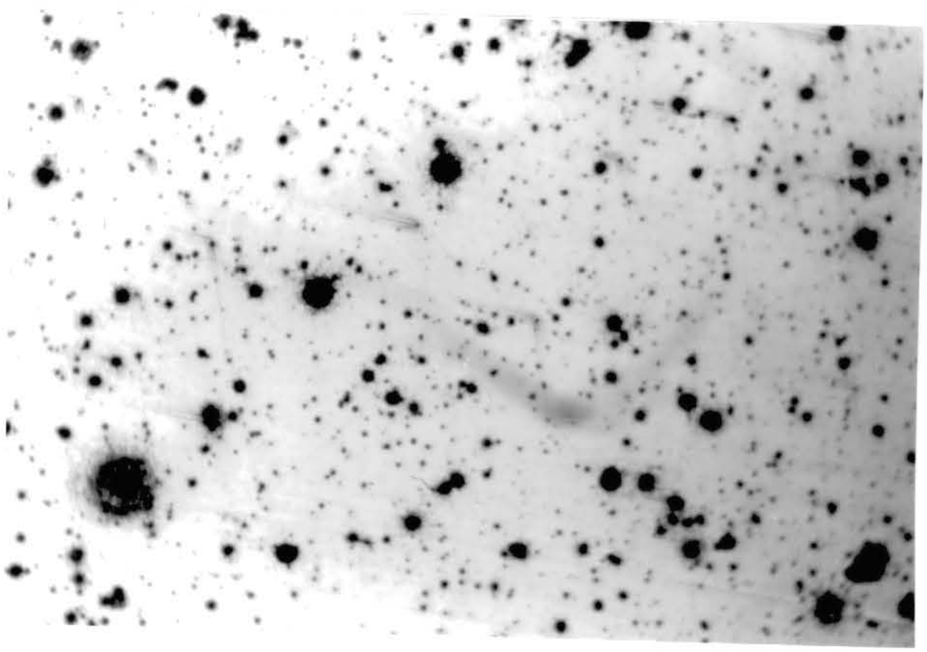
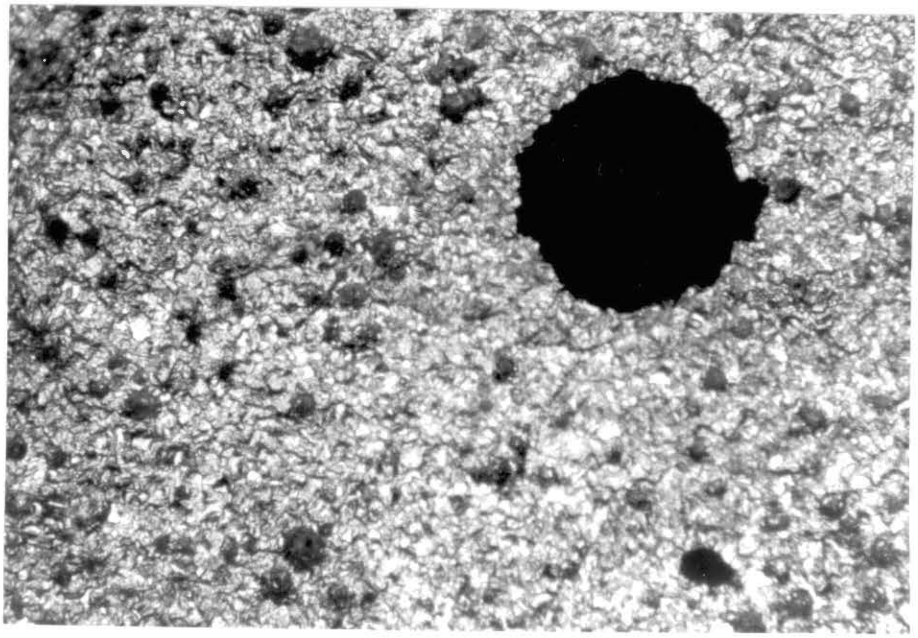
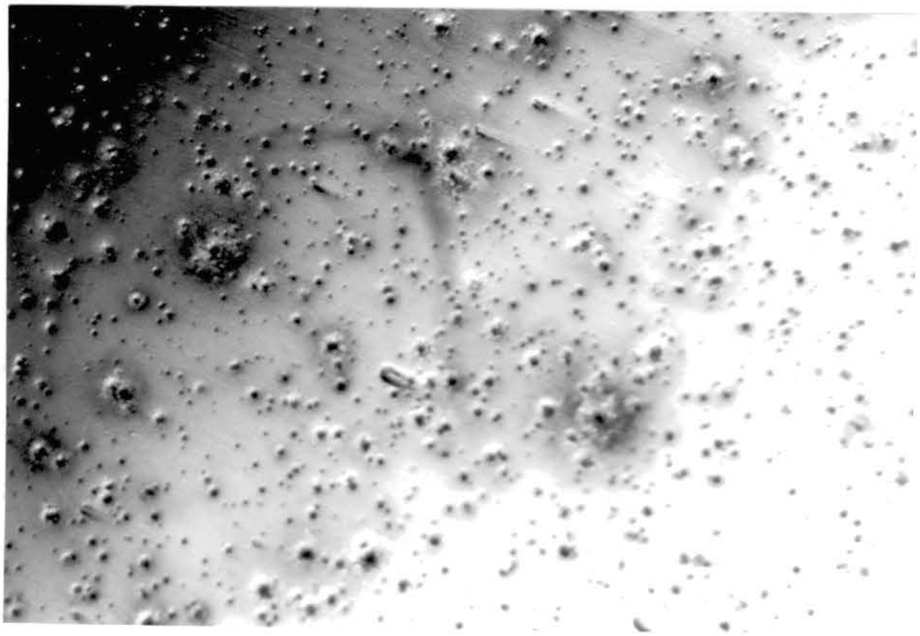


Figure 11. The Pitting Attack of Alloy 600 in 0.01 M Ferric Chloride Solution for 20 hrs at 58 C Shows a General Corrosion (800X)

Figure 12. The Pitting Attack of Alloy 600 in 0.01 M Ferric Chloride Solution for 20 hrs at 24 C Shows Severe Pitting and Close to a General Corrosion (200X)



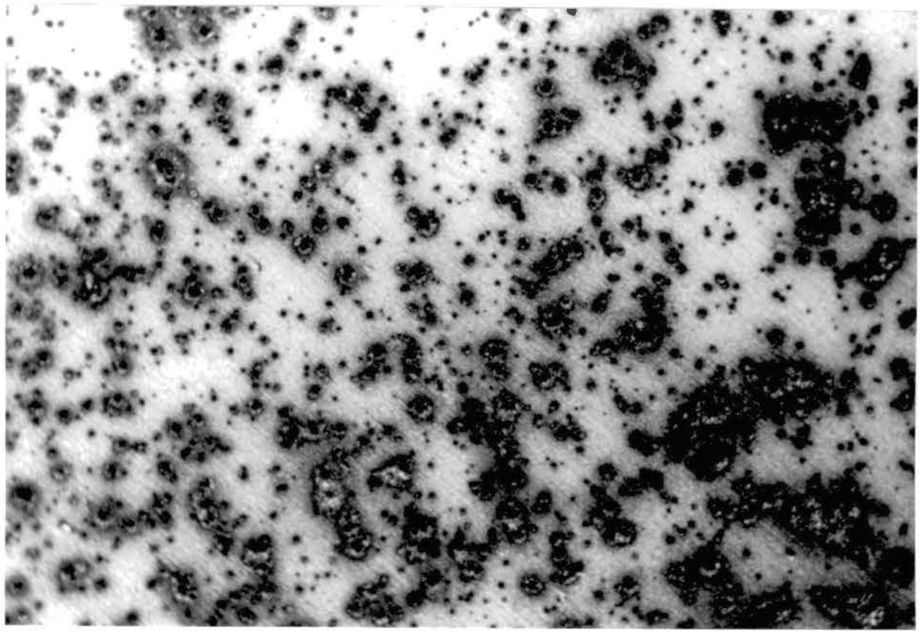


that the critical pitting temperature is lower than 3 C. To follow the early stages of this pitting, the sample of 10 hours at 3 C (figure 13) showed a severe pitting attack as well even it was less severe than the one for 20 hours. Because of this severe pitting attack at early stages, it could be concluded that the critical pitting temperature for Alloy 600 at 0.01 M ferric chloride concentration is much lower than 3 C. For 0.03 M ferric chloride concentration, the 20 hours sample at 3 C (figure 14) showed a considerable pitting attack. To follow the early stages, the 10 hours sample at 3 C (figure 15) showed very few small pits. Consequently, the critical pitting temperature can be concluded at 3 C or slightly below. For 0.1 M ferric chloride concentration, the 20 hours sample at 3 C (figure 16) showed many small pits. To follow the early stages, the 5 hours sample at 3 C (figure 6) showed few small pits, Consequently, the critical pitting temperature could be concluded at 3 C or very close to it.

It is also important to mention that figure 17 showed an IG corrosion as well as pitting corrosion for the sample of 20 hours at 58 C in 0.01 M ferric chloride concentration. This suggests that if the pits do not grow at high temperatures or long times, the severity of pitting attack will be seen as a general corrosion and could attack the grain boundaries and cause this IG attack. A similar observation was noticed by Everhart and Price (11) on Alloy 600 under 0.5 M $CuCl_2$, 1.0 M HF solution.

Figure 13. The Pitting Attack of Alloy 600 in 0.01 M Ferric Chloride Solution for 10 hrs at 3 C Shows an Early Stage of Pitting (200X)

Figure 14. The Pitting Attack of Alloy 600 in 0.03 M Ferric Chloride Solution for 20 hrs at 3 C Shows Many Small Pits (200X)



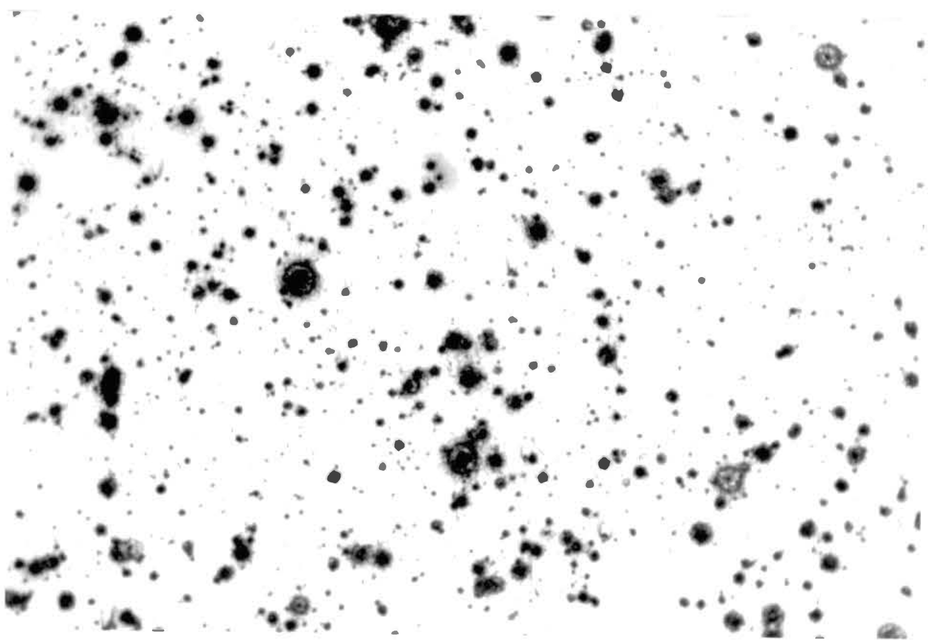
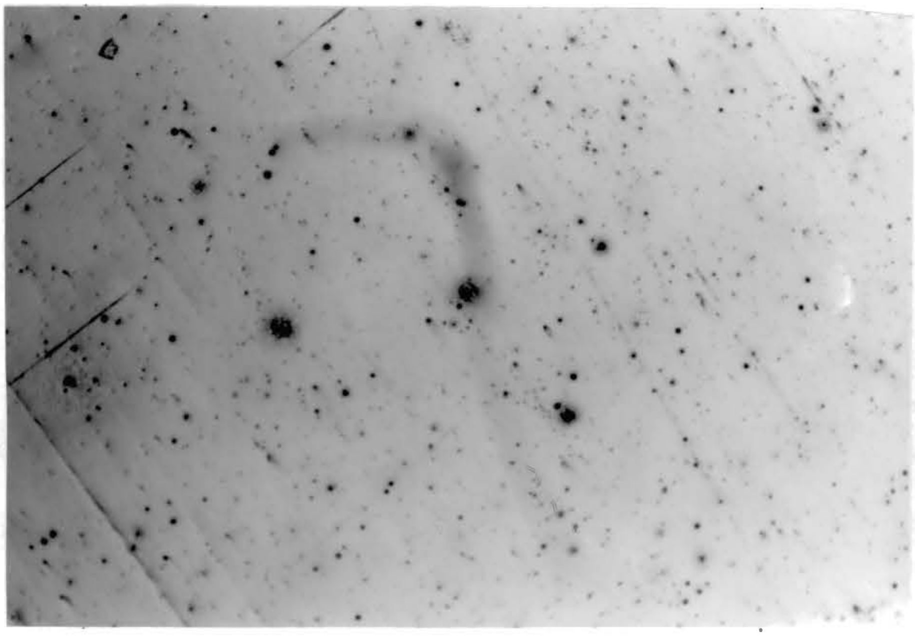


Figure 15. The Pitting Attack of Alloy 600 in 0.03 M Ferric Chloride Solution for 10 hrs at 3 C Shows an Early Stage of Pitting (200X)

Figure 16. The Pitting Attack of Alloy 600 in 0.1 M Ferric Chloride Solution for 20 hrs at 3 C Shows Many Small Pits (200X)



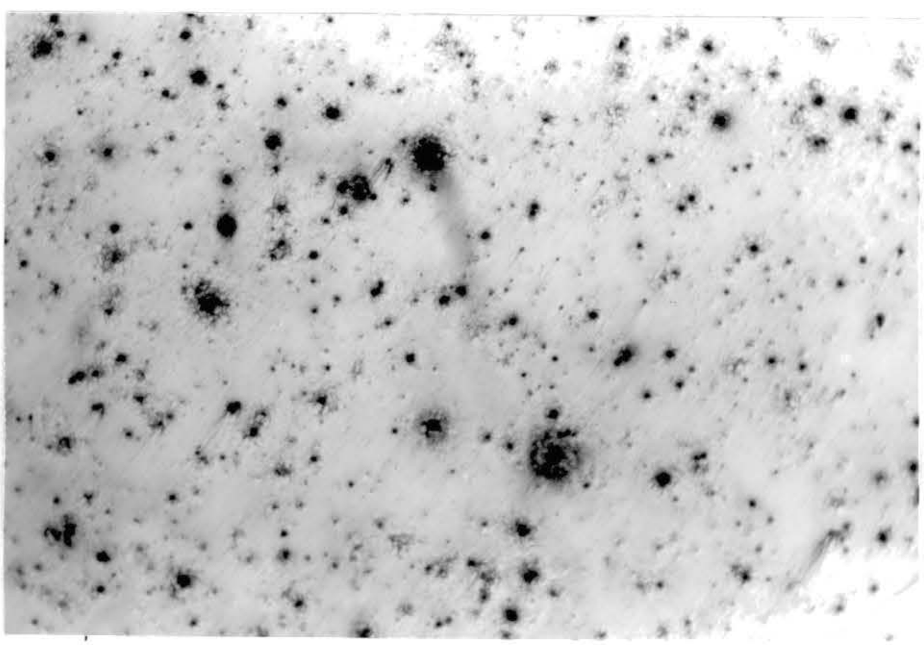
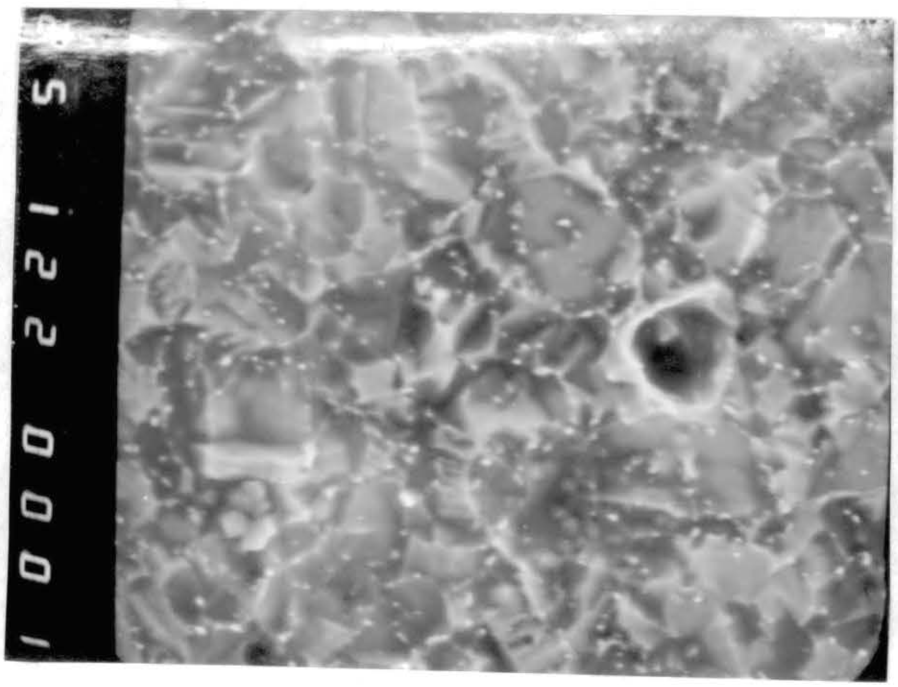


Figure 17. The Pitting Attack of Alloy 600 in 0.01 M Ferric Chloride Solution for 20 hrs at 58 C Shows General Corrosion, Pitting, and IG Attack (1200X)


1000 221 5

Examining the pitting results showed that pit initiation and development could depend mainly on undesirable elements (inclusions) in Alloy 600, the surface finish, and the heat treatment, prior to application.

Park and Smialowska (19) said that Sulfur compounds are often the sites of pits nucleation. Even if the sulfur level is only about 0.008% in Alloy 600, the segregation of sulfur causes sulfide particles to accumulate at the grain boundaries and on the alloy surface which makes the concentration of sulfur greater than in the bulk of the alloy. In addition, the forming of H_2S makes the sulfide ions (SO_4^{2-}) hydrolyse at room temperature, which leads to local depressions (pits) on the surface of the alloy. Consequently, the H_2S evolution will be higher at high temperatures which increases the pits nucleation and their size. Also, it was found that sulfur was absent in the bottom of the pits which leads to belief that sulfur was a pit nucleation site. The chemical reaction (hydrolysis process) between sulfur and H_2O is:

$$S + 4H_2O \longrightarrow SO_4^{2-} + 8H^+ + 6e$$

$$3\,(S + 2H^+ + 2e \longrightarrow H_2S)$$

$$4S + 4H_2O \longrightarrow 3H_2S + SO_4^{2-} + 2H^+$$

This hydrolysis process creates a local acid environment, which locally dissolves the alloy surface and this is considered as pitting initiation.

The anodic reaction consists of metal dissolution in the ferric chloride solution which creates the pits, while the cathodic reaction is the reduction of Fe^{3+} to Fe^{2+} to Fe and O_2 to OH^-. While most of the anodic - cathodic products are soluble in water, chromium oxide is not. Consequently, this chromium oxide would be the corrosion product inside and outside the pits. Since there are hydrogen ions produced during the hydrolysis process, the solution pH is lower inside the pits than the bulk electrolyte. Because the oxide volume is larger than that of the dissolved metal, corrosion products usually get into the pit facet and fill them up. However, the ferric chloride solution will still be able to reach the bottom of the pits and attack the bare alloy, because of the cracks and pores in the layers of corrosion products in the pits. This observation could be attributed to the depth of the pits at long incubation times (19).

Because of the continuing process of nucleation in sulfide sites at the alloy surface at high temperatures and / or long times, pits will contact with each other and eventually produce large pits. For example, the sample of 0.1 M concentration for 5 hours at 58 C (figure 4), and the sample of 0.1 M concentration for 20 hours at room temperature (figure 9).

Surface finish plays a role in the amount of pits on a metal surface. Grooves and scratches are the sites where pit nucleation prefers to start, because of the stagnant condition that these grooves and scratches provide. Furthermore, these sites usually have different mechanical properties compared to the rest of the alloy. Consequently, these sites will corrode faster and eventually the pits become larger and deeper.

Heat treatment also plays a major role in the corrosion resistance ability of Alloy 600. A sensitized heat treatment leads to chromium depletion from the grains and then a precipitation of chromium carbides in the grain boundaries, which make the alloy vulnerable to corrosion. Furthermore, the mechanical properties will be poor. Consequently, these grain boundaries will be the weakest part of the microstructure and will serve as the starting points for pitting nucleation. While, the unsensitized heat treatment eliminates the chromium carbide sites and eventually increases the corrosion resistance of Alloy 600. Furthermore, it is found that the mechanical properties are better than these of the sensitized condition.

It is important to note that two samples of Alloy 600 had been heat treated to both sensitized and unsensitized conditions. Both of them were tested in 0.1 M ferric chloride solution for 24 hours for comparison. The unsensitized sample showed much better pitting corrosion resistance than the sensitized one, which could lead to the belief that the pitting tests were conducted on sensitized samples, since their exact heat treatment was unknown.

Another sample of Alloy 600 had been tested in 0.05 M HCl for 20 hours at room temperature. This sample showed a severe general corrosion. Another sample had been tested in 0.43 M magnesium chloride solution. This sample showed no corrosion, because this chloride solution is not one of the oxidizing acid salts.

SCC Results

The test data can be seen in table III. In this test, the effect of heat treatment on the fractography is shown.

TABLE III

SCC TEST DATA

Test Environment	Condition	Tensile Strength MPa
0.1 M Ferric Chloride	Sensitized	643
0.1 M Ferric Chloride	Unsensitized	675
Liquid Mercury	sensitized	639
Liquid Mercury	Unsensitized	697

In a 0.1 M ferric chloride solution, the sensitized specimen showed two kinds of microstructures, which are IG cracking on the shoulders and microvoids in the neck region (figure 18). Consequently, the fracture is assumed to start by the penetration of the solution from all sides which created the IG cracking (figure 19) in the shoulders and ended in the middle which created the microvoids in the neck region (figure 20). The grains and the grain boundaries showed some pitting attack (figure 21).

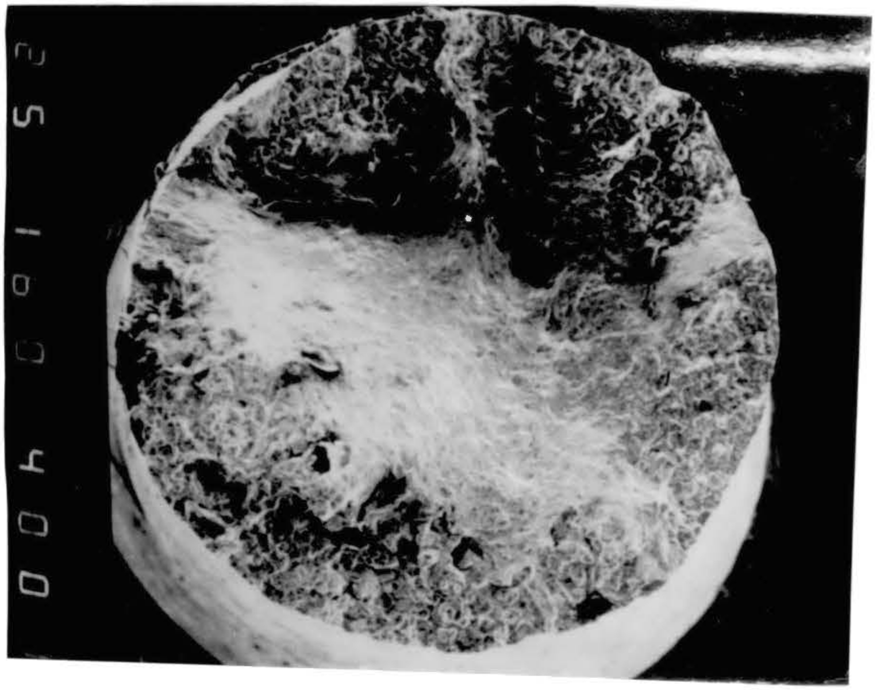
In 0.1 M ferric chloride solution, the unsensitized specimen showed two kinds of microstructures, these are side cracking which is similar to TG cracking on one side of the specimen and microvoids on the rest of the sample (figure 22). Consequently, the fracture is assumed to start by the penetration of the solution from one side and created the TG cracking (figure 23) and ended in the rest of the specimen which created the microvoids (figure 24). There was not any pitting on the specimen.

In liquid mercury, the sensitized specimen showed a full IG cracking microstructure (figure 25) which suggests the aggressive effect of the mercury environment on Alloy 600 (figure 26). The microstructure indicates also that mercury penetrated across the whole cross section which led to no microvoids. The grains and the grain boundaries showed some pitting attack (figure 27).

In liquid mercury, the unsensitized specimen showed a full TG cracking microstructure (figure 28) which again suggests the aggressive effect of the mercury environment on Alloy 600 (figure 29). The microstructure indicates also that mercury penetrated across the whole cross section which

Figure 18. The Fracture Surface in Sensitized Alloy 600 of SCC Test in 0.1 M Ferric Chloride Solution (16X)

Figure 19. The IG Microstructure in Figure 18 in The Shoulder Region (160X)



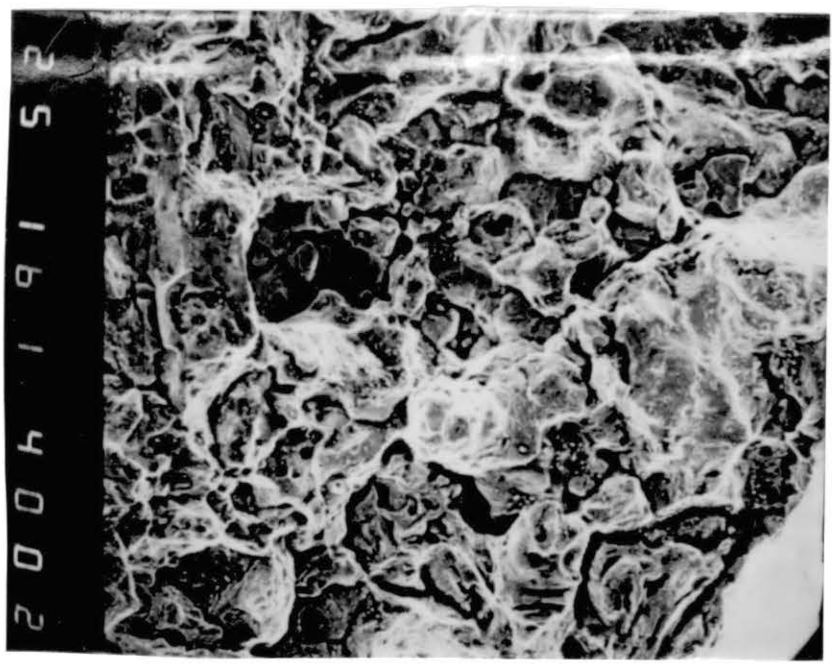
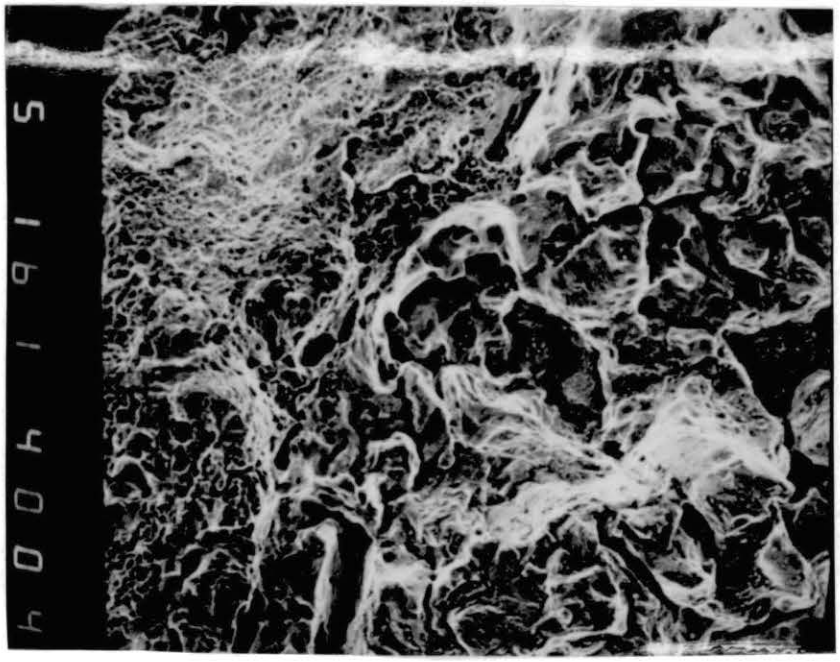


Figure 20. The Microvoids Microstructure in Figure 18 in The Neck Region (160X)

Figure 21. The same as Figure 19 at Higher Magnification Shows a Pitting Attack (800X)



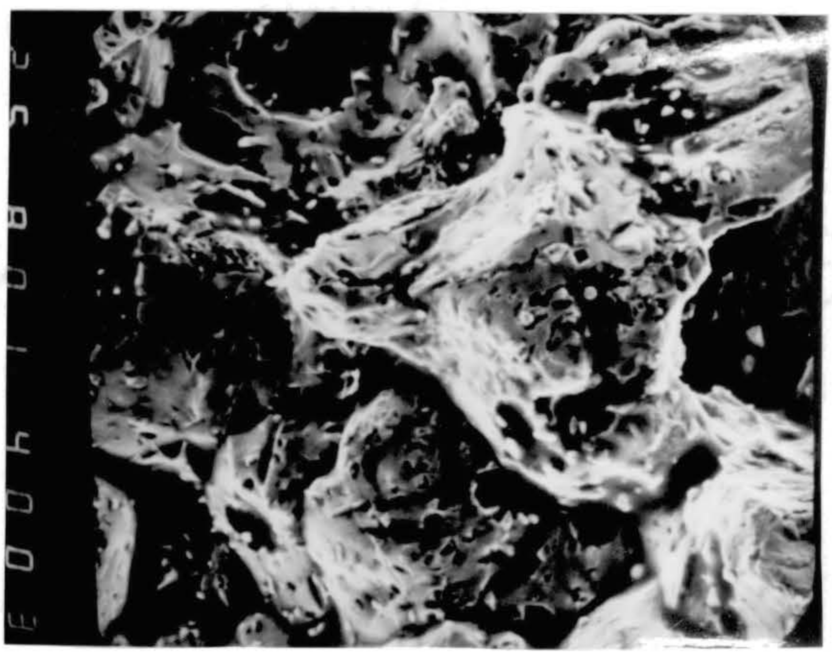
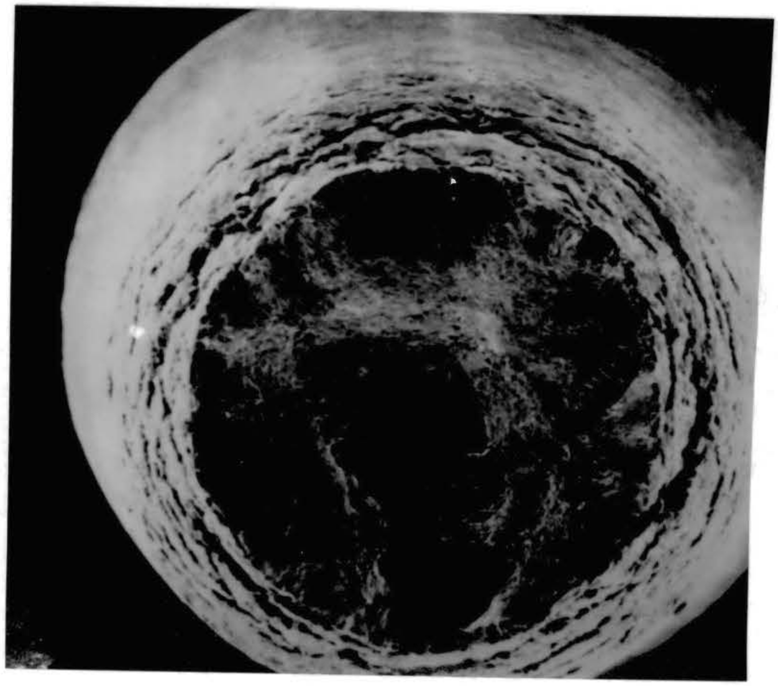


Figure 22. The Fracture Surface in Unsensitized Alloy 600 of SCC Test in 0.1 M Ferric Chloride Solution (16X)

Figure 23. The TG Microstructure in Figure 22 in One Side of The Surface (160X)



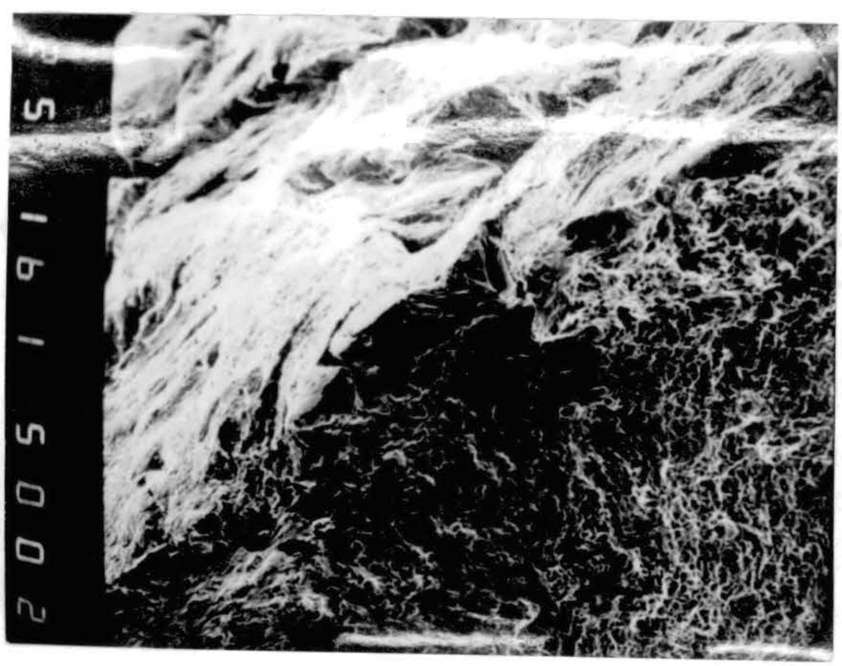
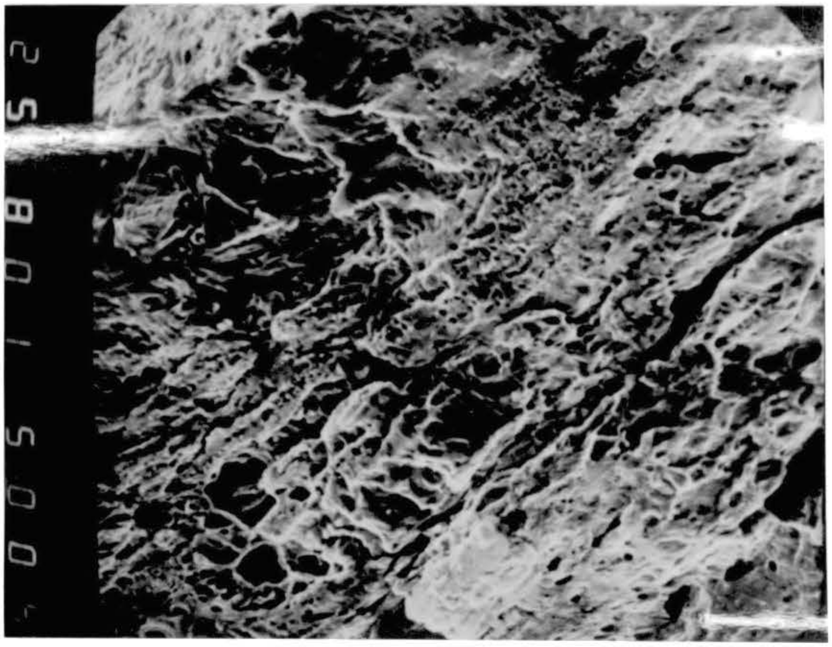


Figure 24. The Microvoids Microstructure in Figure 22 in The Most of The Fracture Surface (800X)

Figure 25. The Fracture Surface in Sensitized Alloy 600 of SCC Test in Liquid Mercury (16X)



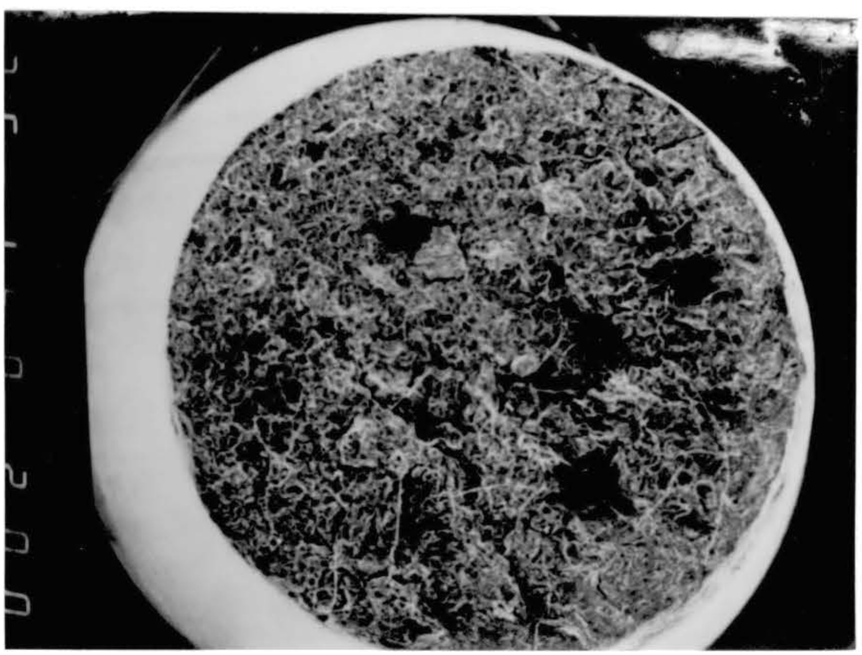
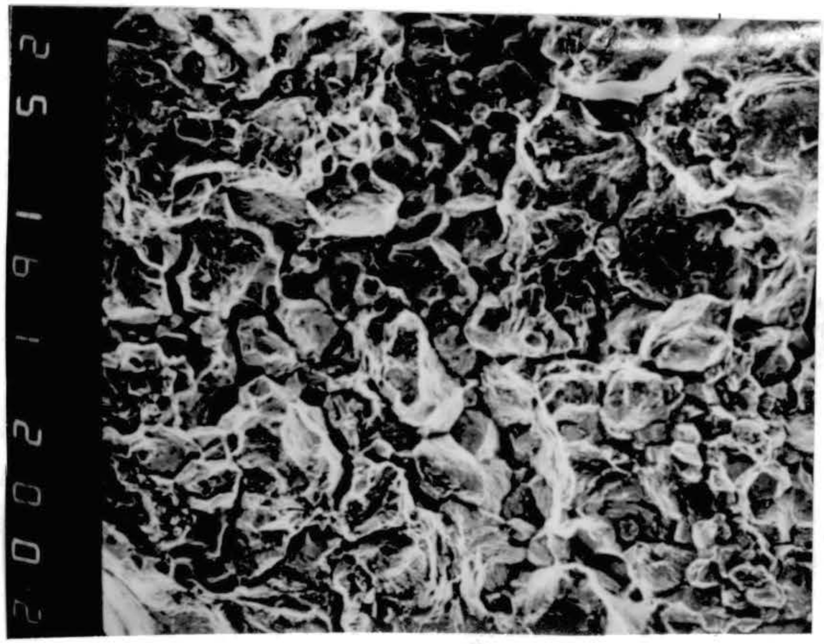


Figure 26. The IG Microstructure in Figure 25 in The Whole Fracture Surface (160X)

Figure 27. The Same as Figure 26 at Higher Magnification Shows a Pitting Attack (800X)



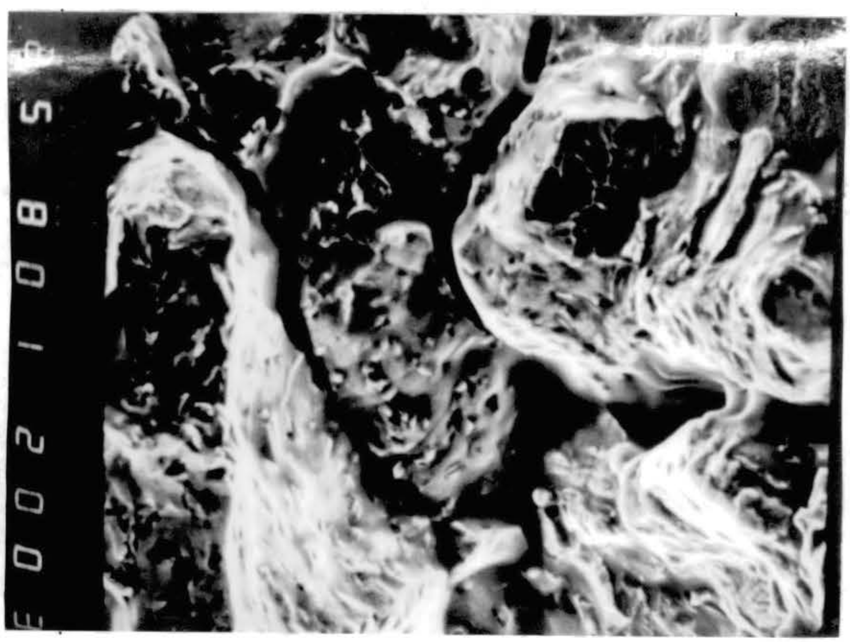
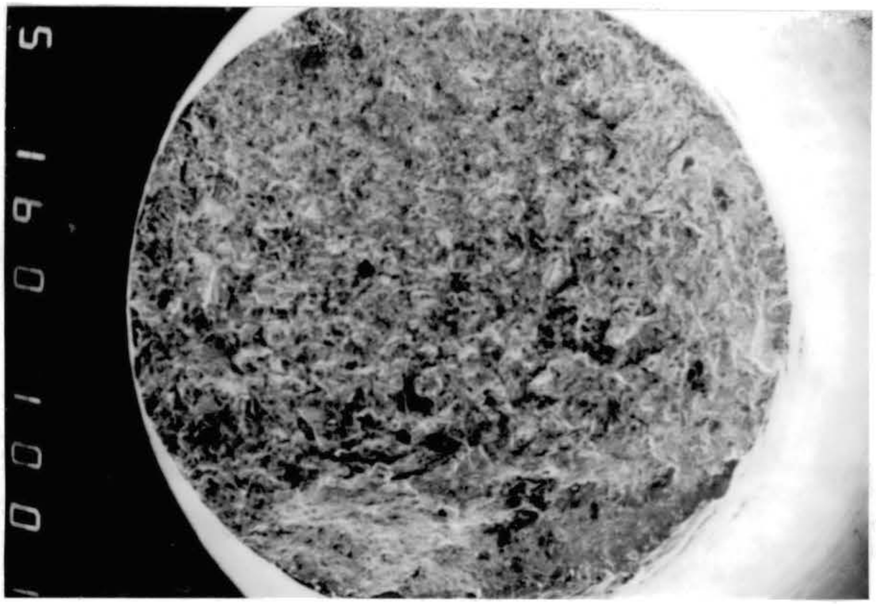


Figure 28. The Fracture Surface in Unsensitized Alloy 600 of SCC Test in Liquid Mercury (16X)

Figure 29. The TG Microstructure in Figure 28 in The Whole Fracture Surface (800X)



led to no microvoids. There was no pitting attack.

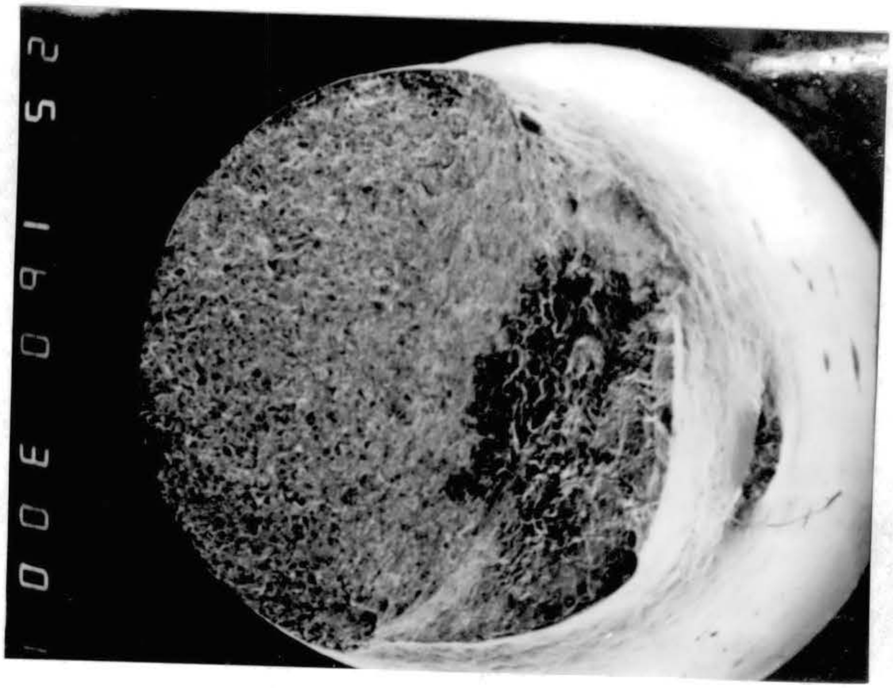
The previous results showed that solutions such as ferric chloride, which cause pitting, can also cause SCC to Alloy 600. Furthermore, pitting could also attack the specimens during the SCC test. However, pitting is associated with SCC only when the specimen in sensitized condition, where the microstructure is IG.

Fatigue Results

The fatigue results of a sensitized specimen in liquid mercury are shown on table IV. The specimen shows two distinct zones, the fatigue zone and the overload zone (figure 30). The fatigue zone consists of an IG microstructure (figure 31) where the fracture started and a transition band. This transition band consists of two microstructures which are IG and TG (figure 32). It was noticed that the IG microstructure showed a lot of thick grain boundaries precipitation (figure 33), where it was not the case in SSTs. Also, the TG microstructure shows some tearing and secondary cracks, where in the SSTs there was none. The fracture ended in the overload zone, which followed the TG microstructure of the transition band. The overload zone consists of microvoids (figure 34).

Figure 30. The Fracture Zone in Sensitized Alloy 600 of the Fatigue Test in Liquid Mercury Shows The Fatigue Zone and The Overload Zone (16X)

Figure 31. The IG Microstructure in Figure 30 in The Fatigue Zone (160X)



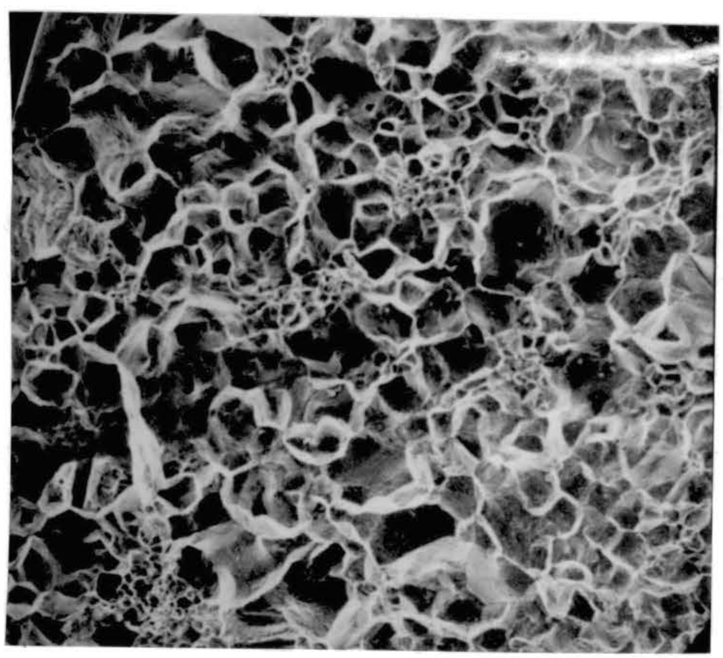
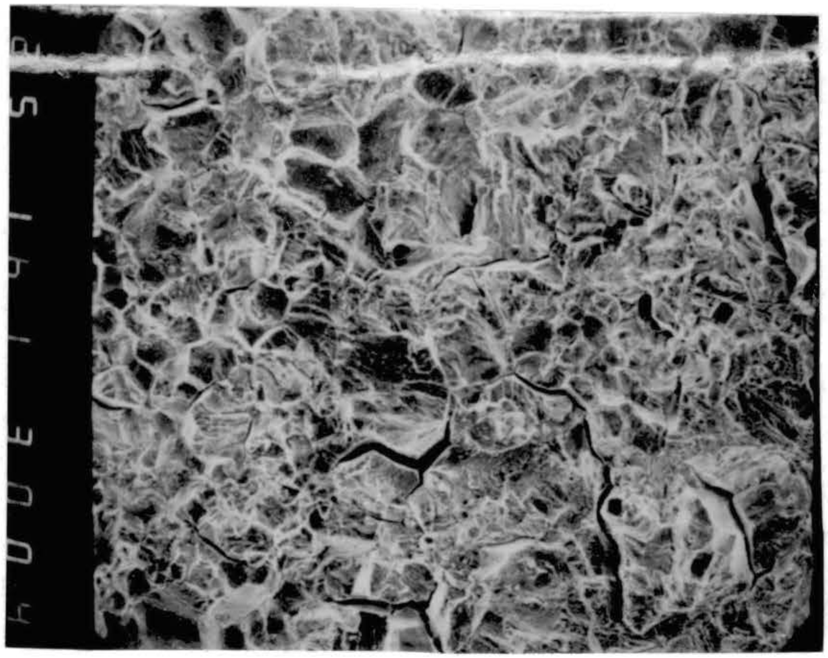


Figure 32. The Transition Band Region in Figure 30 in The Center of The Fracture Zone Shows IG and TG Microstructures (160X)

Figure 33. The IG Microstructure in Figure 30 at Higher Magnification Shows The Grain Boundaries Precipitation (800X)



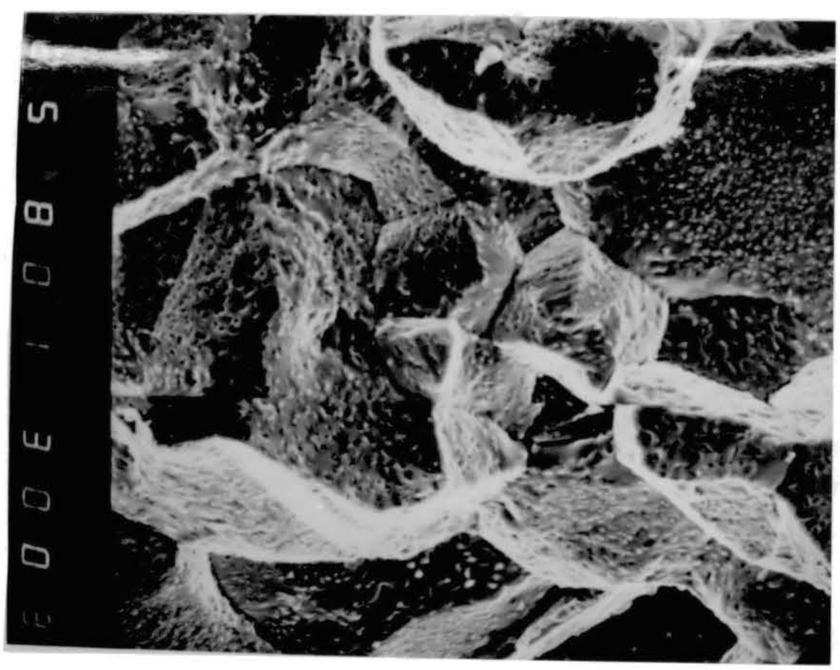


Figure 34. The Microvoids Microstructure in Figure 30 in The Overload Zone (160X)

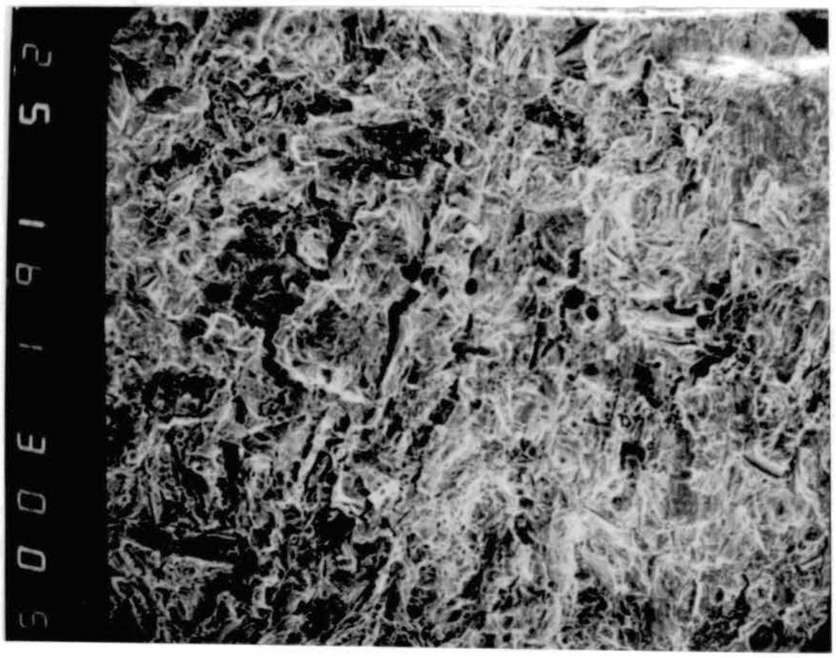


TABLE IV

FATIGUE TEST DATA

Test Environment	Condition	Fatigue Stress MPa	Cycles to Failure
Mercury	sensitized	404	128600

Correlation Between Pitting and SCC

Upon studying both the pitting and SCC results, the ferric chloride solution caused not only pitting, but SCC as well. For example, the 0.1 M ferric chloride solution that caused pitting corrosion in pitting tests also caused SCC in the SSTs, as described before.

Upon studying the photos of the SSTs results in the 0.1 M ferric chloride solution, the sensitized specimen showed many pits on the grains which were visible due to the IG attack. This IG attack was shown on the starting stages of the fracture on both sides of the sample (figure 18) with pits on the grains and the grain boundaries of the IG attack (figure 21), which led to the fracture of the sample at a later stage. The fracture ended with a microvoids on the center of the sample (figure 20) where there is a pit - free zone.

Upon studying the photos of the unsensitized specimen tested in 0.1 M ferric chloride solution, the specimen showed no pits. It comprised side cracks with a broken structure, which is similar to a TG attack (figures 23). The fracture started with these broken up structure on one side of the sample and ended with microvoids on the rest of the sample (figure 22), with no indication of pitting. Upon studying the photos of the SSTs in liquid mercury, the results were similar to those of the 0.1 M ferric chloride solution. The sensitized specimen showed full scale IG attack, with pits on the grains (figure 27), while the unsensitized specimen showed a full scale of TG attack with no pits (figure 29).

The IG microstructure in these results is always associated with sensitized heat treatment which is a sign of brittle fracture that gives bad mechanical properties as well as poor corrosion resistance. As a result of that, Alloy 600 is vulnerable to pitting corrosion in a ferric chloride solution and many other environments.

In the unsensitized state, the microstructure is TG which is a sign of ductile fracture that gives good mechanical properties as well as good corrosion resistance. As a result of that, Alloy 600 is not vulnerable to pitting corrosion in many environments.

CHAPTER VII

DISCUSSION

Alloy 600 has many sensitive applications such as power stations and nuclear reactors (14). The corrosion failure of this alloy in chloride environments creates a lot of attention.

Pitting results showed that any increase of ferric chloride concentration has a devastating effect on pitting resistance of the alloy. As a result of that, the number and / or size of pits increases with the increase of the concentration for the same incubation time. Because of that, Alloy 600 can survive longer times in service at lower concentrations before it gets pits.

Increasing the incubation time can also increase the number and / or size of pits. However, pitting corrosion can become general corrosion at longer time (figures 11,17). It is important to note that samples of Alloy 600 usually corrode within a few hours in ferric chloride solutions, which is considered a severe corrosive environment. This observation could make the incubation time a minor factor in this case and more important in less severe environments.

Temperature is a major factor on pitting resistance. Generally, increasing the temperature can cause increasing in the number and / or size of pits. However, Alloy 600 could show higher corrosion resistance at higher temperatures, because of the transpassive behavior of this alloy as it is shown in figures 7,3,8. The same thing has been observed by Park and Szklarska (19) in other solution. This specific property can be utilized in specific applications for longer life service. Although, Alloy 600 is recommended at higher temperatures (10,14,15,19), it should be used under less corrosive environments.

Cleaner versions and surfaces of Alloy 600 play a major role in increasing the pitting corrosion resistance of Alloy 600, since the pitting usually starts at the inclusions. Beside of the inclusions, some elements in Alloy 600 should be reduced for better pitting corrosion resistance, such as sulfur and copper.

There was a sample tested in 0.43 M magnesium chloride solution at room (24 C) and high temperature (58 C), but no corrosion attack was observed. That is because Alloy 600 has very good corrosion resistance (1 mpy (0.025 mm/yr)) to none oxidizing acid salts, even in the form of chloride (14,18). So, not every chloride solution can cause pitting, only those oxidizing acid salts such as ferric chloride, cupric chloride, and mercuric chloride.

The effect of heat treatment on pitting resistance is very sensitive. The results showed that the sample of sensitized heat treatment showed more pits than the unsensitized sample, because of the precipitation of chromium carbides at the grain boundaries which leaves the grains lacking chromium and then less corrosion resistance. In fact, the unsensitized sample showed very good corrosion resistance compared to the sensitized one which could enhance life service for longer time. Consequently, given the sensitive application of Alloy 600, this observation can be a big factor in safety and endurance.

Immersing Alloy 600 for a long time at higher temperatures could cause severe pitting and / or general corrosion as well as preferential grain boundary attack (figure 17). However, this pitting attack did not clearly outline the grain boundaries. Stress will be needed to outline the grains and the grain boundaries, which was shown in the SCC tests.

In the SCC tests, the heat treatment was a major factor in determining the behavior of the alloy and consequently the resultant microstructure. In general, the sensitized condition of Alloy 600 led always to IG cracking in both ferric chloride solutions and liquid mercury. This IG cracking suggests brittle behavior of the alloy. The presence of stress during the SSTs caused the grain boundaries to be visible. On the other hand, unsensitized Alloy 600 showed always TG cracking in both solutions. This TG cracking suggests ductile behavior of the alloy. Because of the plastic deformation that occurred before the TG cracking, the slip bands became the higher energy sites and a transition to TG cracking occurred. So, the heat treatment should be checked before utilizing Alloy 600, because any crack created on the surface of the sensitized alloy will penetrate the surface without blunting and eventually causing fast and brittle fracture. By contrast, the unsensitized condition is promising since the fracture was ductile. This means that if any crack is created on the surface of the unsensitized alloy, it will blunt and create a plastic deformation zone which causes any crack to stop penetrating, which eventually prevents or delays failure during service.

There was a difference in fractography between LME, HE, SCC, and Fatigue in Alloy 600. SCC tests in both ferric chloride solution and liquid mercury showed no sign of mixed mode IG and TG cracking in either the sensitized or unsensitized conditions, because the effective heat treatment which prevented the specimens from not being fully sensitized or not fully unsensitized. Each condition showed a distinct microstructure. The sensitized condition showed only IG cracking in both solutions, while unsensitized condition showed only TG cracking in both solutions. In contrast, both HE and LME showed mixed mode of IG and TG attack in the necked regions and IG attack in the shoulder regions of the samples. However, the mixed mode of IG and TG cracking was only seen in specimens held at elevated temperatures for a long time, while the other heat treated specimens showed only IG cracking. The other difference between HE, LME, and SCC was that there was no pitting attack on the grains in HE and LME tests, because these environments are not corrosive in that aspect, while there was a pitting attack in the sensitized specimens of SCC tests.

There was also a difference in fractography between fatigue tests in hydrogen and liquid mercury of Price and Good (20) and fatigue tests in liquid mercury of this thesis. The test of this thesis showed a larger IG fracture zone and consequently, less TG fracture zone, because this sample was sensitized, while the others were not. However, the fractography in liquid mercury of this thesis was similar to the one of Price and Good where both have some tearing and secondary cracking. Consequently, the differences with hydrogen fractography is the same as shown in chapter III.

Finally, it is also important to mention that the same environments that cause pitting can also cause SCC in Alloy 600 such as ferric chloride. It is also true for other nickel base alloys (11). In addition, pitting attack was seen on the grains after SCC tests in ferric chloride solution and mercury in sensitized condition. Since the chromium was depleted from the grains and precipitated in the grain boundaries in sensitized specimens, the grains would be vulnerable to pitting corrosion. This would cause a reduction in corrosion resistance of the sensitized specimens. On the other hand, there was no pitting corrosion in unsensitized specimens, because there was no chromium depletion. Therefore, the unsensitized specimens have very good corrosion resistance. It is worth mentioning that the presence of stress during SSTs cause the grain boundaries to become anodic with respect to the adjacent areas, which causes a decrease in pitting attack compared with pitting tests with no stress, especially in sensitized samples.

CHAPTER VIII

CONCLUSIONS

1. Ferric chloride solutions can cause severe pitting corrosion as well as SCC in Alloy 600. The severity of the corrosion attack increases with increasing solution concentration, incubation time, and temperature.

2. Not every chloride solution can cause corrosion to Alloy 600 only the oxidizing acid salts, which ferric chloride is one of them, can cause that attack. For example, magnesium chloride did not cause any kind of corrosion at any concentration, because this chloride is not an oxidizing acid salt.

3. Different chloride solutions cause different severity of pitting attack because of the different oxidation power of each solution. This can be concluded by studying the results of Alloy 600 in cupric chloride (19), NaCl (15), and others (20). However, ferric chloride is more severe than the others by comparing the results with each other.

4. The heat treatment is a major factor in pitting corrosion resistance. Unsensitized samples has higher corrosion resistance than sensitized samples.

5. Judging from the pitting results, it could be concluded that all the received pitting samples were in

sensitized condition. That is because even the samples were cold worked previously, the sensitized temperature range (538 - 760 C) is very close to be a part of the heat treatment that precede the cold work during manufacturing or after.

6. In SCC tests, the heat treatment was a major factor to the outcome of the fractography. A sensitized heat treatment caused complete IG cracking in both ferric chloride solution and liquid mercury, which suggests the brittle behavior of the alloy. By contrast, an unsensitized heat treatment caused complete TG cracking in both solutions which suggest the ductile behavior of the alloy.

7. There is a difference in fractography between SCC and both LME and HE tests. Both LME and HE shows mixed mode of IG and TG in necked regions and IG in shoulder regions, while SCC shows only one mode.

8. The only difference in fractography between the fatigue test of this thesis and fatigue tests of Price and Good (20) is that IG fracture zone is larger in this thesis than the one of them, because the specimen of this thesis is sensitized.

9. In SCC tests, the sensitized specimens showed some pitting attack on the grains, because of the reduction in corrosion resistance due to the chromium depletion from the grains and the precipiation of chromium carbides in the grain boundaries. While the unsensitized specimens showed no sign of pitting attack, because there was no reduction in

corrosion resistance.

10. The unsensitized condition is a favorite heat treatment to Alloy 600, because it increase both pitting corrosion resistance and SCC susceptibility which, eventually increases the life service of Alloy 600.

A SELECTED BIBLIOGRAPHY

1. American Society For Metals, Metal Handbook, 9th edn, Vol. 3, Metal Park, Ohio, 1980, pp. 142-172.

2. American Society For Metals, Metals Handbook, 9th edn, Vol. 13, Metal Park, Ohio, 1980, pp. 641-650.

3. A.S.T.M., and A.I.M.E., Symposium on Stress-Corrosion Cracking of Metals, Philadelphia, 1944.

4. Bandy, R., R. Roberge, and R. C. Newman, "Low Temperature Stress Corrosion Cracking of Inconel 600 Under Two Different Conditions of Sensitization", Corrosion Science, Vol. 23, No. 9, 1983, pp. 995-1006.

5. Bandy, R., R. Roberge, and R. C. Newman, "Low Temperature Stress Corrosion Cracking of Sensitized Inconel 600 in Tetrathionate and Thiosulfate Solutions", Corrosion, Vol. 39, No. 10, 1983, pp. 391-398.

6. Bandy, R., and D. Van Rooyen, "Effect of Thermal Stabilization on Low Temperature Stress Corrosion Cracking of Inconel 600", Corrosion, Vol. 40, No. 6, 1984, pp. 282-289.

7. Bandy, R., and D. Van Rooyen, Corrosion of Nickel Base Alloys, American Society For Metals, Metal Park, Ohio, 1986, pp. 117-126.

8. Briant, C. L., C. S. O'toole, and E. L. Hall, "The Effect of Microstructure on The Corrosion and Stress Corrosion Cracking of Alloy 600 in Acidic and Neutral Environments", Corrosion, Vol. 42, No. 1, 1986, pp. 15-27.

9. Choi, D. and G. S. Was, "Pit Growth in Alloy 600/690 Steam Generator Tubes in Simulated Concentrated Environments (Cu^+, Cl^-, and SO_4^{2-})", Corrosion, Vol. 46, 1990, pp. 100-111.

10. Crum, J. R., "Stress Corrosion Cracking of Inconel 600 and 690 Under High-Temperature Caustic Conditions", Corrosion, Vol. 42, 1986, pp. 368-372.

11. Everhart, L. G., and C.E. Price, "Stress Corrosion Cracking in Alloy 400 (UNS NO4400) at Room Temperature", Corrosion Testing and Evaluation, Silver Anniversary Volume, ASTM STP 1000, 1990, pp. 000-000.

12. Fontana, M. G., Corrosion Engineering, Mcgraw-Hill, Inc., New York, 1986.

13. Friend, W. Z., Corrosion of Nickel and Nickel-Base Alloys, Jone Wiley and Sons, Inc. 1980.

14. Handbook of Huntington Alloy Products of the International Nickel Company, Inc., Inconel 600, Tech. Bull. Huntington, West Virginia, 1969.

15. Karaminezhaah-Rajbar, M. J. Mankowskie, and D. D. Macdonald, "Pitting Corrosion of Inconel 600 in High Temperature Chloride Solution Under Controlled Hydrodynamic Conditions" Corrosion, Vol. 41, No. 4, 1985, pp. 197-204.

16. Kekkonen, T., and H. Hanninen, "The Effect of Heat Treatment on The Microstructure and Corrosion Resistance of Inconel X-750 Alloy", Corrosion Science, Vol. 25, 1985, pp. 789-803.

17. Lee, K. H., G. Crangnolind, and D. D. Macdonald, "Effect of Heat Treatment Applied Potential on The Caustic Stress Corrosion Cracking of Inconel 600", Corrosion, Vol. 41, No. 9, 1985, pp. 540-553.

18. Mogerman, W. D., and F. L. Laque, Nickel, Monel, Inconel, The international Nickel Company, Inc., New York 1950.

19. Park, J. R., and Z. Szklarska - Smialowska, "Pitting Corrosion of Inconel 600 in High Temperature Water Containing $CuCl_2$." Corrosion, Vol. 41, No. 11, 1985, pp. 665-675.

20. Price, C. E., and J. K. Good, "The Fractography of Hydrogen and Mercury Embrittlement in Inconel 600", J. Materials Engineering, Vol. 9, 1987, pp. 283-291.

21. Roelandt, A., and J. Vereecken, "A Modified Electrochemical Technique (Electrochemical Potentiokinetic Reactivation) For Evaluating The Susceptibility of Inconel 600 to Intergranular Cracking", Corrosion, Vol. 42, No. 5, 1986, pp. 289-298.

22. Szklarska-Smialowska, Z., D. Grimes, and J. Park, "The Kinetics of Pit Growth on Alloy 600 in Chloride Solutions at High Temperatures", Corrosion Science, Vol. 27, No. 8, 1987, pp. 859-867.

VITA

IHSAN ALI HUSSEN

Candidate for the Degree of

Master of Science

Thesis: CORROSION ASPECTS OF ALLOY 600

Major Field: Mechanical Engineering

Biographical:

Personal Data: Born in Arbil, Iraq, August 9, 1964, the son of Ali Hussen Ibraheem and Majda Ahmed Saleh.

Education: Graduated from Al-Mamoon High School, Baghdad, Iraq, in June 1978; received Bachelor of Science Degree in Mechanical Engineering from University of Baghdad in July 1987; completed requirements for the Master of Science degree at Oklahoma State University in May, 1991.

Professional Experience: Teaching Assistant, Department of Mechanical Engineering, Oklahoma State University, January, 1991, to May, 1991.