

## Corrosion Fatigue of Alloys Containing Chromium and Molybdenum

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### ABSTRACT

*Corrosion fatigue test results indicate that the fatigue life of IN600, IN601 and C22 specimens tested in 3.5 % sodium chloride solution are essentially the same as for specimens tested in air. Test results also showed that for IN600, IN601 and C22 alloys, the number of cycles to failure was highest in air and sodium chloride solution, followed by specimens fatigued in hydrochloric acid, and was least in specimens fatigued in ferric chloride solution. No evidence of surface pitting was found on C22 specimens in all three solutions, whereas IN600 and IN601 were both pitted. However, pits were generally larger in IN600 likely due to lower Cr content than in IN601.*

**KEYWORDS** – IN600, IN601, C22, HCl, FeCl<sub>3</sub>, corrosion, fatigue, solution.

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Date of Submission: Date, 11 June 2013



Date of Publication: Date 25 June 2013

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### I. INTRODUCTION

The amount of Cr and Mo in those nickel-based alloys used in environments, in which corrosive media are present, has a significant effect on their corrosion properties [1-5]. The current study was undertaken to determine the effect of the Cr and Mo content on the corrosive and corrosion fatigue behavior of three nickel-based alloys, IN600, IN601 and C22 immersed in 3.5%NaCl solution, concentrated HCl and 10%FeCl<sub>3</sub> solution. The addition of Cr to Ni-based alloys changes the nature of the surface from nickel oxide to a more corrosive resistant one comprised largely of chromium oxide. The addition of Mo to nickel-based chromium alloys also increases the corrosion resistance and often increases the resistance to pitting and crevice corrosion. The three alloys have similar yield and ultimate tensile strengths [3-6].

Fatigue crack initiation in corrosive media has been attributed to various factors such as pitting corrosion sites, stress concentrations and specimens dimensions. Increased corrosion fatigue enhanced deformation was proposed to explain the apparent intensification of intrusions and extrusions in materials [7-10]. These mechanisms and their interactions with fundamental fatigue processes have recently become of interest to many researchers since little is actually known about the fundamentals of environment/cyclic loading interactions.

Fatigue is the time-dependent growth of subcritical cracks under cyclic (repeated) loading [6-13] and is one of the most common causes of failure of engineering structures; it is often undetected, unexpected and could be catastrophic. Considerable engineering efforts over the past century have been devoted to the characterization and understanding of the mechanisms of fatigue. Such understanding is essential to service life prediction, planning of in-service inspections, development of better fatigue resistant materials, better component design, improved manufacturing processes, and optimum material selection. Fatigue failures have been the subject of engineering studies for more than a century [7].

Simultaneous exposure of alloys to aggressive environments and cyclic stresses often results in a degradation of fatigue resistance. Even laboratory air containing some moisture has been shown to influence crack propagation rates of materials when compared with those obtained from tests in vacuum or in dehumidified inert gases. Measures to avoid such corrosion cracking include careful materials selection, heat treatment, and modifications of material/environment interactions through coating, controlled solution chemistry, inhibition, and applied potentials. This is of extreme importance in several technologies, including turbine blades for jet engines, heat exchangers, nuclear waste containment, and chemical plant pipelines.

Extensive studies are necessary to characterize the corrosion fatigue of materials in aggressive environments. The process of corrosion fatigue is quite complex since there are many mechanical, environmental and metallurgical variables that contribute to the process of corrosion fatigue [8]. This

complexity frustrates attempts to develop a thorough understanding of the individual contributions of each mechanism to the corrosion fatigue cracking process.

It is not the intent of the research described in this paper to examine in detail the exact fracture mechanisms involved in the corrosion fatigue of the alloys studied or to determine which of the twenty five or so mechanisms may be operative. Rather, to determine the effect on corrosion fatigue of IN600, IN601 and C22 of two of the most harsh and aggressive corrosive environments, concentrated hydrochloric acid (HCl) and ferric chloride acid (10%FeCl<sub>3</sub>) at pH 0.

## II. EXPERIMENTAL PROCEDURE

The three nickel based chromium alloys used in this study and their chemical compositions are presented in Table 1. Corrosion rate for the three alloys in HCl and in FeCl<sub>3</sub> solutions were calculated prior to corrosion fatigue test (Table 1) and (table 2) respectively. Corrosion fatigue tests were performed under two stress levels (480 MPa and 532 MPa) and three test conditions: (1) fatigued in air, (2) precorroded (soaked in solutions from 4 to 7 hours then dried and fatigued in air), and (3) fatigued in the two corrosive solutions.

Table 1 Chemical compositions of three Ni-based alloys (wt.%).

Chemical compositions (wt.%).					
Alloy	Ni	Cr	Fe	Mo	C
IN600	Bal.	15.77	8.58	-	0.05
IN601	Bal.	22.14	16.09	-	0.3
C22	Bal.	21.42	2.95	13.67	0.003

Table 2 Corrosion rate of three Ni-based alloys in concentrated HCl solution

HCl solution at pH 0.0		
Alloy	$I_{corr}$ (nA/cm <sup>2</sup> )	Corrosion rate (mm/year)
IN600	1.20E+04	0.13
IN601	1.1 X 10 <sup>4</sup>	0.12
C22	900	0.010

Table 3 Corrosion rate of three Ni-based alloys in 10%FeCl<sub>3</sub> solution

10%FeCl <sub>3</sub> solution at pH 0.0		
Alloy	$I_{corr}$ (nA/cm <sup>2</sup> )	Corrosion rate (mm/year)
IN600	7.00E+06	76.7
IN601	5.8 X 10 <sup>2</sup>	0.006
C22	70	0.0008

The test was conducted using high-capacity servohydraulic fatigue testing machines. Fatigue test specimens were machined from the as received materials as shown in Figure 1. The test specimen was mounted between the actuator and the load cell by screwing it into the test fixture. Details of the corrosion cell configurations and dimensions are shown in Figure 2. An O-ring was installed at the bottom of the cell to permit transfer of force to the specimen while preventing leakage of the solution as shown in Figure 3.



Figure 1. Fatigue test specimen before testing.

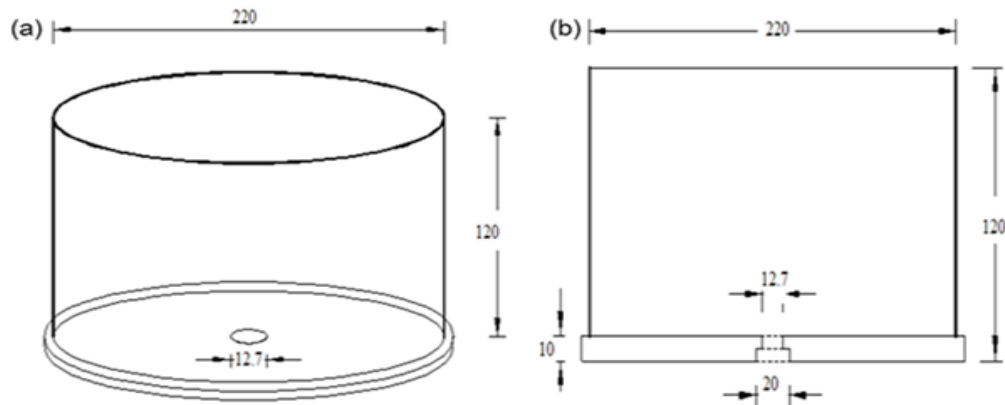


Figure 2. Schematic design of corrosion cell (a) Dimensions of corrosion cell and (b) Cross section in (mm)

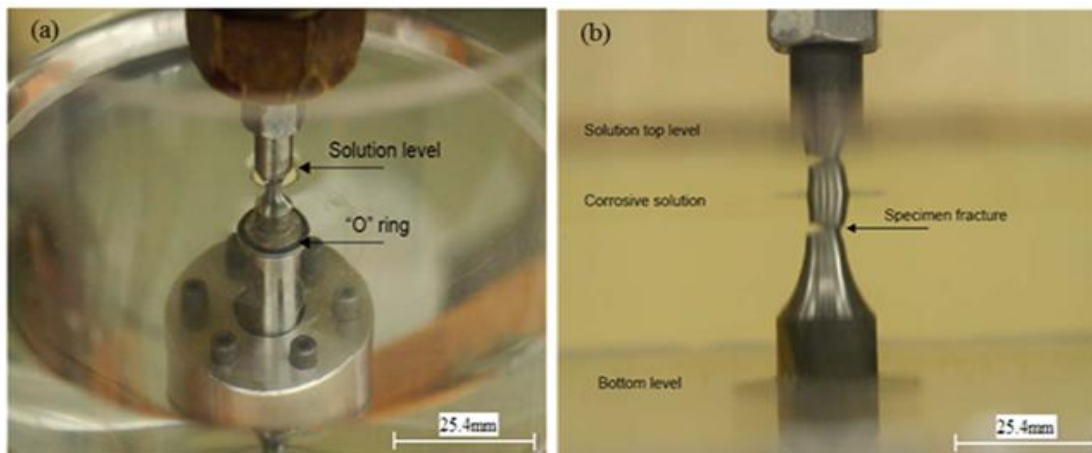


Figure 3. Fatigue test system: (a) specimen before fracture with O-ring installed, and (b) specimen after

fracture. In this investigation, fracture surface morphology was examined with a scanning electron microscopy (SEM) to determine crack initiation sites and crack propagation using and these observations correlated to the corrosion fatigue strength.

### III. RESULTS AND DISCUSSIONS

Figures 4 and 5 show that, in general, the number of cycles to failure for all the alloys tested was highest for fatigue testing in air without pre-corrosion, lower for pre-corroded specimens fatigue tested in air, and lowest for specimens fatigue tested in a corrosive environment without pre-corrosion. More detailed observations follow.

The fatigue results for IN601 immersed in HCl at pH = 0.0 presented in Figure 4 (b) show that the corrosive environment has an effect on the fatigue life of the specimen. In contrast, the specimens pre-corroded for 4 hours exhibited the largest (average) fatigue life, and the specimens tested in air also had a higher fatigue life than in the corrosive environment.

The fatigue results for alloy C22 given in Figure 4 (c) show that the corrosive environment reduced fatigue life, while the fatigue life of specimens tested in air after 6 hours of pre-corrosion is higher than the results for the specimens fatigue tested in the HCl solution. In both cases fatigue tests ran for an average of about 6 hours (200,000 cycles at 36,000 cycles per hour).

The fatigue results for IN600 tested in 10 wt. % FeCl<sub>3</sub> solution at pH = 0.0 in Figure 5 (a) show that the fatigue life for the specimens fatigue tested in this solution were shorter than those for specimens pre-corroded for 7 hours prior to testing in air. The standard deviations in the data from the fatigue testing are shown in Figure 6 and are seen to be quite similar as between the three different alloys and testing conditions.

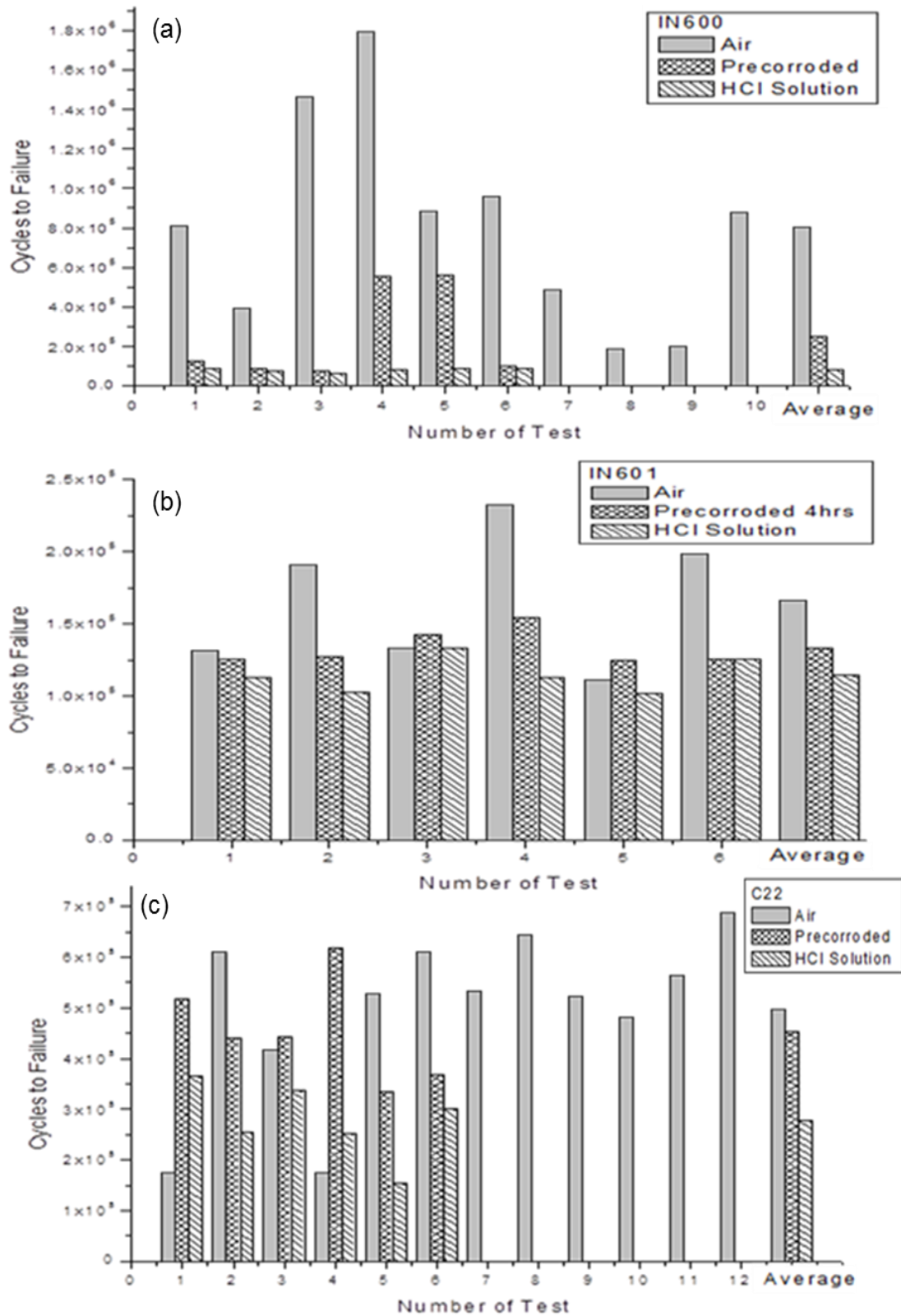


Figure 4. Effect of pre-corrosion and a concentrated HCl solution at pH 0 on fatigue behavior of (a) IN600 at 480MPa, (b) IN601 at 532MPa, and (c) C22 at 532MPa.

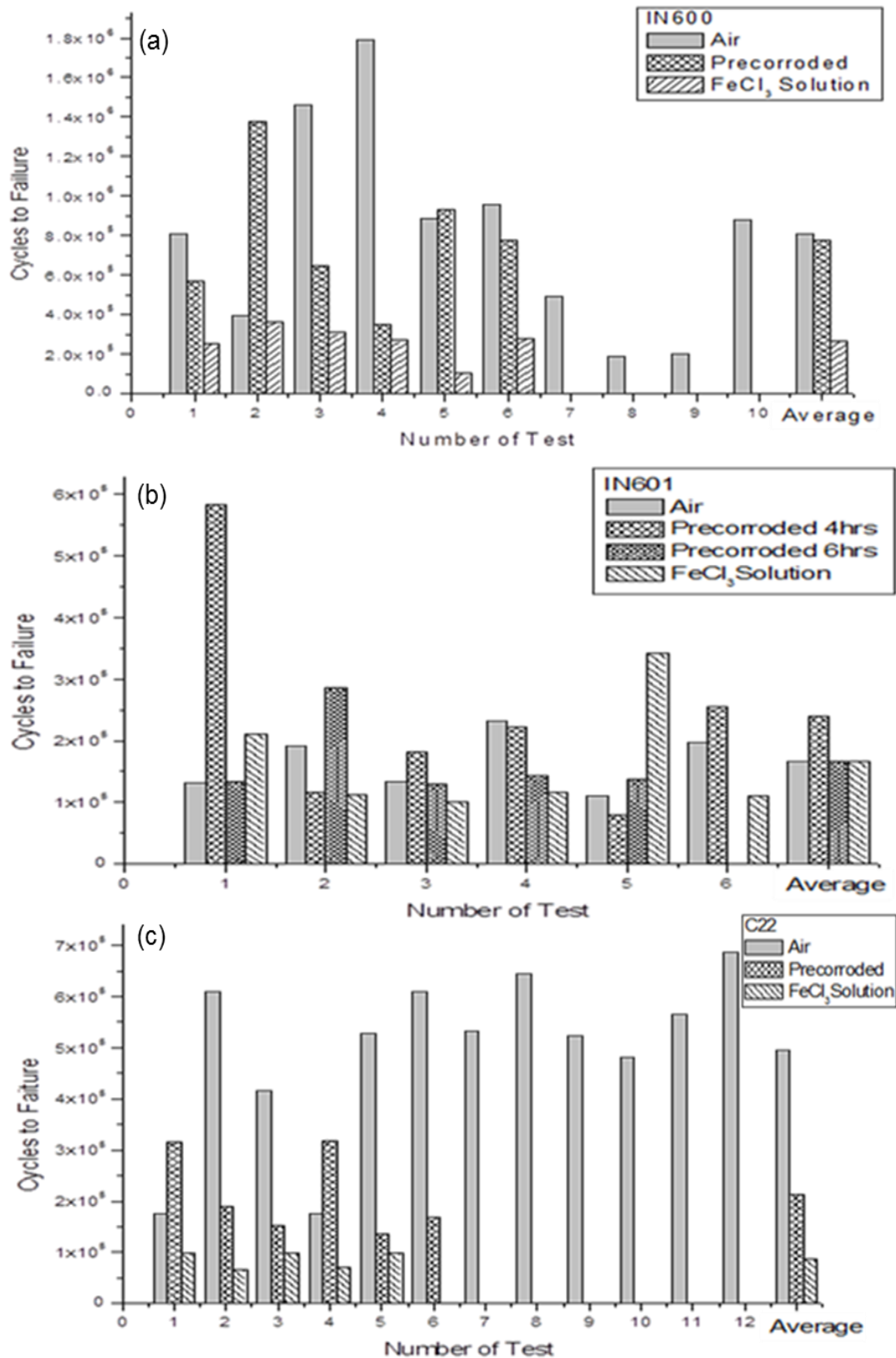


Figure 5. Effect of pre-corrosion and 10 % FeCl<sub>3</sub> solution at pH 0 on fatigue behavior of (a) IN600 at 480MPa, (b) IN601 at 532MPa, and (c) C22 at 532MPa.

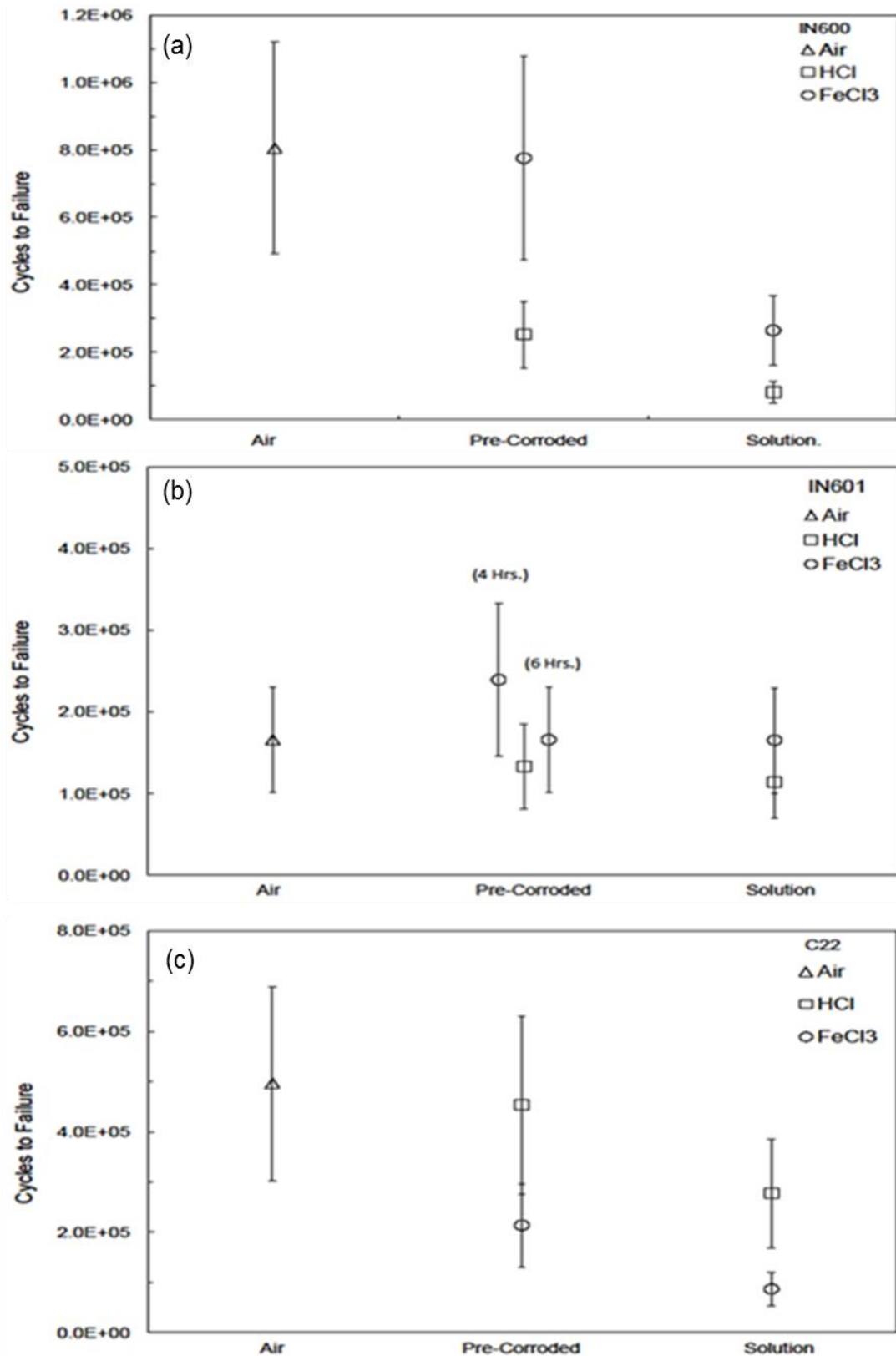


Figure 6. Standard deviations of fatigue test results at pH 0: (a) IN600, (b) IN601 and (c) C22.

The information on standard deviations is particularly significant because these fatigue tests lasted about 7 hours, a similar time that was required for fatigue failure of specimens in solution (about 250,000 cycles at 36,000 cycles per hour).

For IN600, the corrosion rate in 10 wt. %  $\text{FeCl}_3$  solution at  $\text{pH} = 0.0$  is very high, 27 mm/year. It is obvious that such a high corrosion rate would greatly affect the fatigue life if tests were conducted over a time frame of weeks or months instead of the tests of the few hours of this study.

The fatigue results for IN601 in 10 wt. %  $\text{FeCl}_3$  solution at  $\text{pH} = 0.0$  as presented in Figure 5 (b) show that the pre-corrosion in solution has a great effect on the fatigue life of IN601. The fatigue life is similar to that obtained for IN601 in an HCl solution at  $\text{pH}$  of 0.0 and is indicative of both the toughness and the corrosion resistance of this alloy.

The fatigue results for alloy C22 in 10 wt. %  $\text{FeCl}_3$  solutions at  $\text{pH} = 0.0$  are presented in Figure 5 (c) which shows that pre-corrosion for 7 hours followed by fatigue testing in air has about the same effect as fatiguing in solution. (The fatigue life in solution is about 200,000 cycles / second). It may therefore be concluded that for alloy C22 in 10 wt. %  $\text{FeCl}_3$  solution at  $\text{pH} = 0.0$  there is an interaction between the solution and the alloy at the crack tip.

The test results indicate that for both alloys IN600 and C22 there is an interaction between the corrosive HCl and  $\text{FeCl}_3$  solutions and the alloy at the fatigue crack tip which shortens the fatigue life over that of specimens pre-corroded for a similar length of time. Further, the fatigue life of IN601 is not greatly affected by the presence of HCl solution or 10 wt. %  $\text{FeCl}_3$  solution at  $\text{pH}$  of 0.0 (either diverging pre-corrosion or corrosion in solution). This result is quite unexpected as it follows the expected trend of corrosion resistance increasing with Cr and Mo content. It is the author's opinion that in this particular study the IN601 was not as greatly affected in the pre-corroded specimens in the two aggressive environments as IN600 and C22, due to the higher carbon content in IN601 compared to IN600 and C22. When IN601 is subjected to the corrosive environments used in this research carbide is formed at surface pits. This carbide creates a hardened surface and improves strength (Figure 5 (b)) even though the surface is pitted. It is assumed that the carbide is localized within the pits.

Figure 7 shows a representative specimen surface prior to any fatigue testing. In Figure 8 (a), surfaces for IN600 fatigued in air after pre-corrosion in HCl solution at  $\text{pH}$  of 0.0 reveal many large surface pits. IN601, Figure 8 (b), shows smaller and fewer pits and alloy C22 exhibits only a few small pits (Figure 8 (c)). These results are consistent with the fatigue test results which show a large effect of corrosion for IN600 and much smaller effects for IN601 and alloy C22.

The specimen surface for IN600 fatigued in air after pre-corrosion in 10 wt. %  $\text{FeCl}_3$  solution at  $\text{pH} = 0.0$  exhibited extensive pitting as shown in Figure 9 (a). Fewer pits were observed for IN601 (Figure 9 (b)) and almost no pits for alloy C22 (Figure 9 (c)). This data again indicates the inherent strength due to higher carbon content in 601 compared to IN600 and C22. Also, for alloy C22 the reduction in fatigue strength must result from an interaction between the metal and the  $\text{FeCl}_3$  solution at the fatigue crack tip since there is little surface pitting to initiate the fatigue crack.

The resistance to corrosion fatigue for the alloys studied here is in proportion to the amount of alloying elements, particularly Cr, Mo, Co and W. Alloy IN600, with the least corrosion fatigue resistance, has only 25 % alloying elements. IN601, with 40% alloying elements, has better resistance, and alloy C22 with 49 % alloying elements has the greatest resistance.

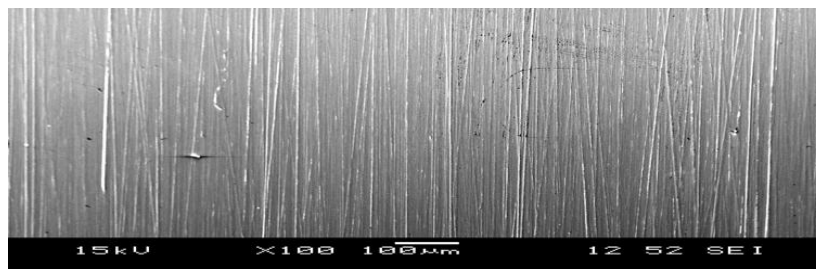


Figure 7. A representative specimen surface prior to any fatigue testing.

The specimen surface for alloys fatigue tested in concentrated HCl solution at  $\text{pH}$  of 0.0 and  $\text{FeCl}_3$  solution at  $\text{pH}$  of 0.0 are shown in Figure 10 and Figure 11 respectively. The results are similar to those for the pre-corroded specimens. IN600 exhibits numerous pits (Figure 9 (a)), IN601 fewer pits (Figure 9 (b)), and alloy C22 very minor pits (Figure 9 (c)).

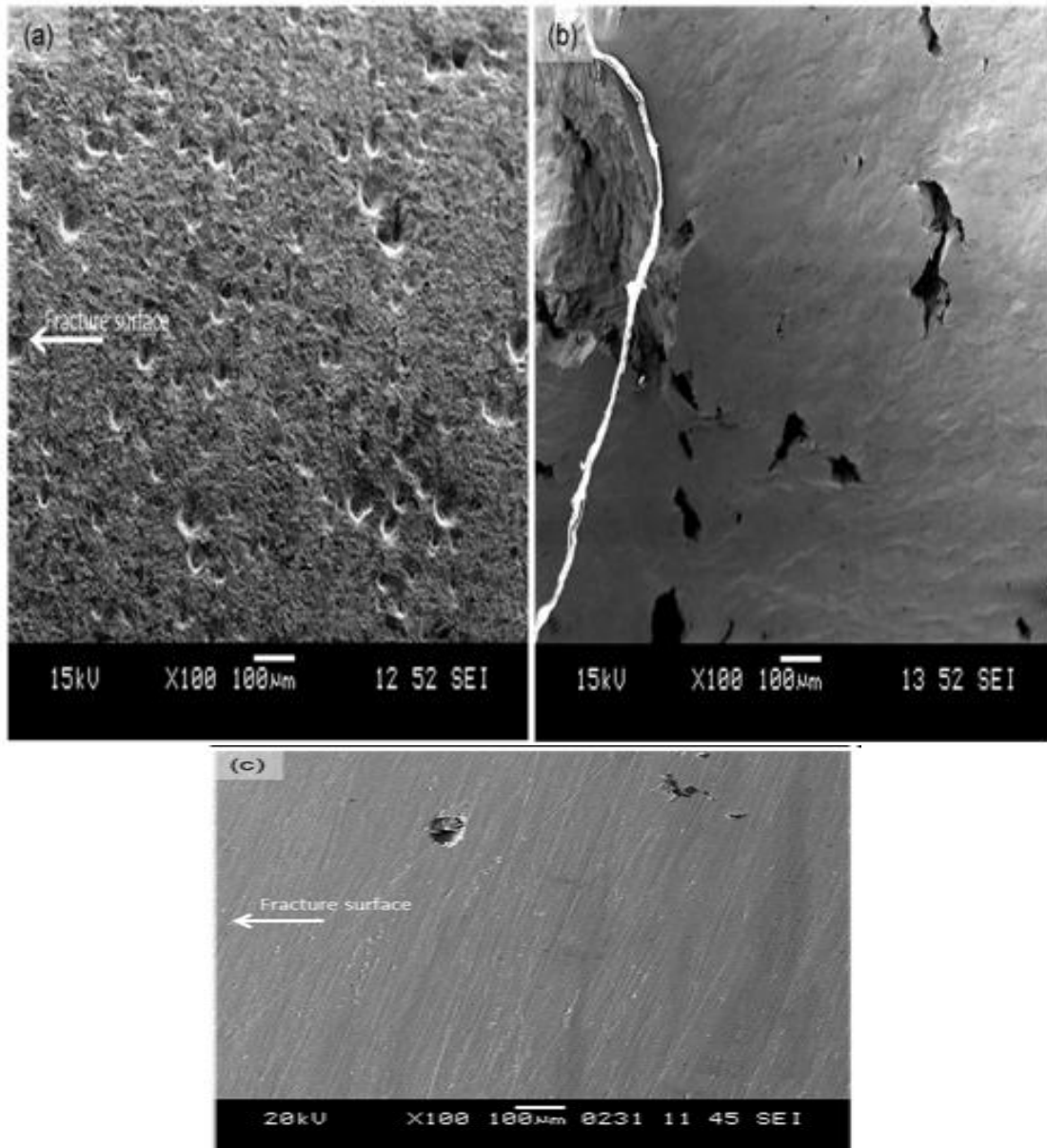
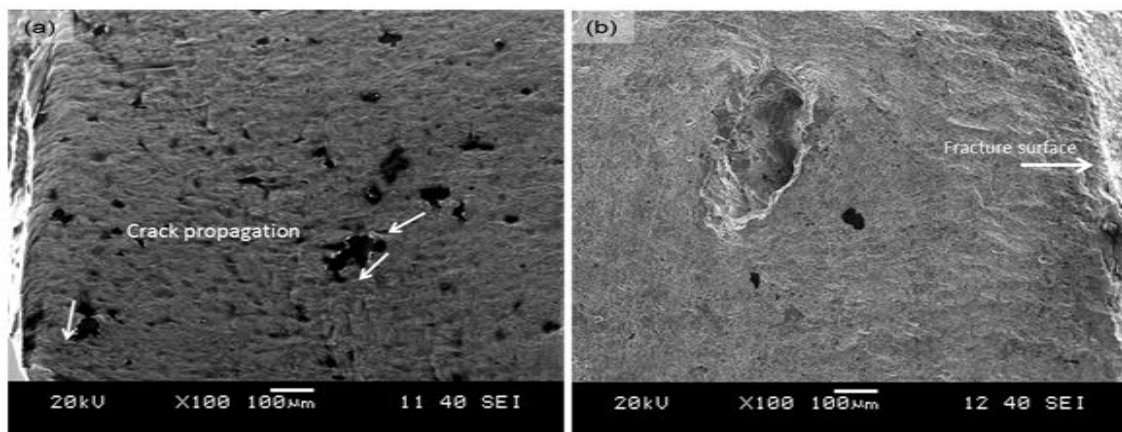


Figure 8. Pits near the fracture surface after pre-corrosion in concentrated HCl solution at pH 0: (a) IN600 for 13 hrs, (b) IN601 for 4hrs, and (c) C22.





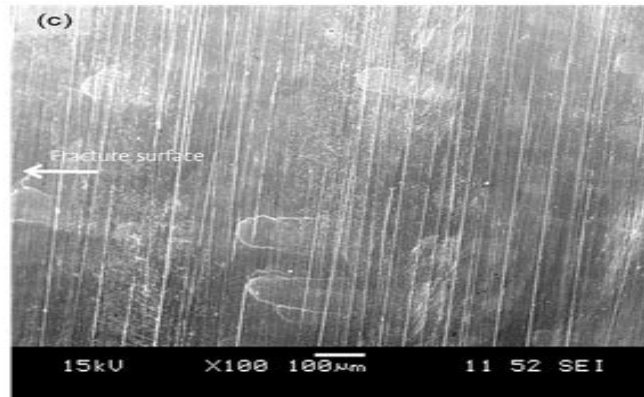


Figure 9 Pits near the fracture surface after pre-corrosion formed by 10% FeCl<sub>3</sub> solution at pH 0: (a) IN600, (b) IN601, and (c) C22.

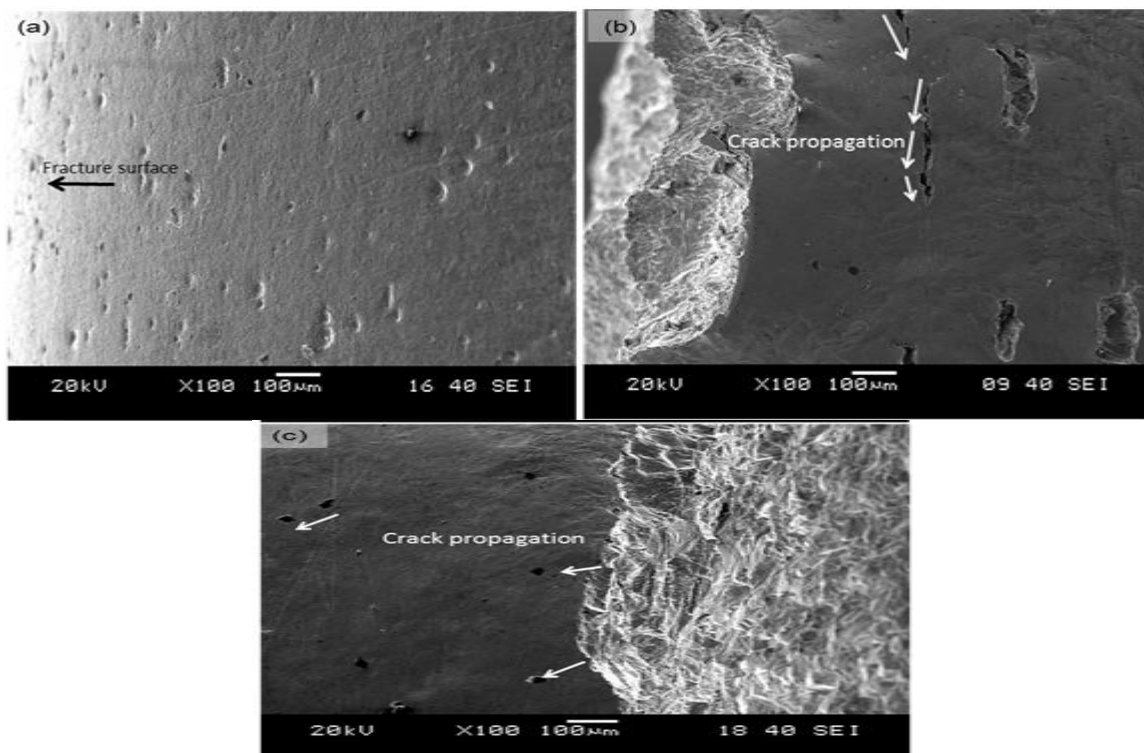
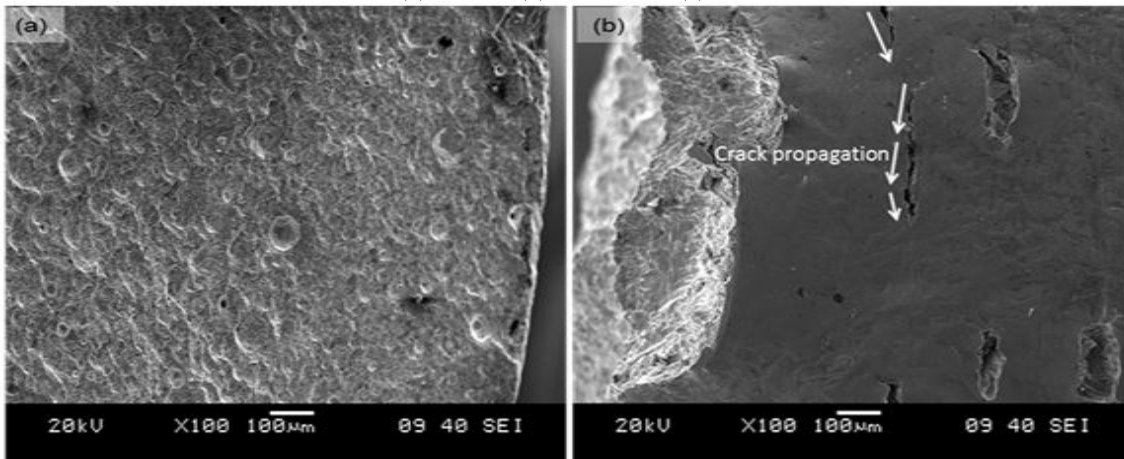


Figure 10. Corrosion pits near the fracture surface after specimen fatigued in concentrated HCl solution at pH 0: (a) IN600, (b) IN601 and (c) C22.



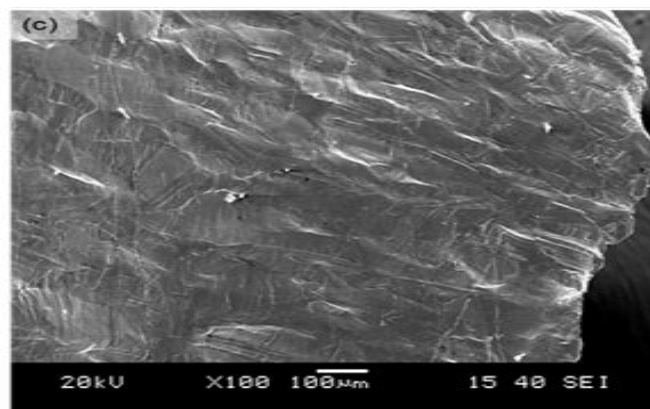


Figure 11. Corrosion pits near the fracture surface after being fatigued in 10% FeCl<sub>3</sub> solution at pH 0 (a) IN600, (b) IN601, and (c) C22.

For 10%FeCl<sub>3</sub> solution at pH of 0.0, IN600 exhibits numerous pits (Figure 11 (a)), IN601 fewer pits (Figure 11 (b)), and alloy C22 almost no pits (Figure 11 (c)). The corrosion resistance of IN601 is likely due to its high chromium content (22.14%), since it is well known that Cr forms a very protective, corrosion resistant Cr<sub>2</sub>O<sub>3</sub> oxide layer.

Extensive corrosion pits formed by aggressive environments (HCl) and (10%FeCl<sub>3</sub>), such as those in Figure 10 and Figure 11, respectively, may occur at carbide sites or inclusions and appear to be larger closer to the fracture zone (plastic zone). One can observe pits adjacent to fracture zone pits extended from one pit to another adjacent pit while specimens were undergoing fatigue. Each pit becomes a site of crack nucleation with the crack propagating to the next pit and so on, one after the other, until final fracture (Figures 10 and 11).

IN600 has the lowest amount of Cr (15.77%Cr) as compared to the other two alloys, IN601 and C22. This might explain the shorter fatigue life of IN600 as also indicated in corrosion rate (Table 2) and (Table 3). Generally, pitting corrosion was most severe when specimens were fatigued in solution and less than those fatigued in air

The main reason for adding Mo to an alloy is to enhance repassivation behavior. This behavior can be attributed to the formation of Mo oxide during pitting or the enrichment of Mo metal at the alloy surface. The Mo-containing oxide film formed at the specimen surface can prevent the further growth of the pit and decrease acidity in the pits as also indicated in corrosion rate data (Table 2) and (Table 3).

It can be concluded that pits which formed on specimens fatigued in 10 wt. % FeCl<sub>3</sub> solution affect fatigue life more than pits formed in the HCl solution. Hence, when these three alloys are considered for fatigue applications in aggressive corrosive environments, alloy C22 would be considered superior.

#### IV. CONCLUSION

A conclusion section must be included and should indicate clearly the advantages, limitations, and possible applications of the paper. Although a conclusion may review the main points of the paper, do not replicate the abstract as the conclusion. A conclusion might elaborate on the importance of the work or suggest applications and extension IN600 exhibited the least corrosion resistance of the three alloys studied. In 10 % FeCl<sub>3</sub> solution at pH = 0.0, the corrosion rate was estimated at 77 mm / year compared to slightly under 1.0 mm / year for both alloys IN601 and C22.,

For the IN600 exposed to pre-corrosion in HCl and FeCl<sub>3</sub> solution at pH = 0.0 a considerable decrease in fatigue life over the non-pre-corroded specimens was noted. However, the fatigue life for specimens tested in these solutions was even lower than those pre-corroded specimens and fatigued in air and suggested that there is an interaction between the metal and the solution at the fatigue crack tip.

IN601 did not experience a decreased fatigue life for either specimens that were pre-corroded or tested in solutions specimens as compared to specimens fatigued in air. This observation provides evidence of the inherent corrosion resistance of IN601. IN601 is also inherently “tough“, since surface damage due to corrosion has a low effect on the short term high cycle fatigue life.

Pre-corroded and fatigued-in-air alloy C22 specimens exhibited a decrease in fatigue life over specimens fatigued only in air. This result indicates some surface damage as a result of pre-corrosion even though pitting was minimal. All C22 specimens fatigued in solution exhibited a fatigue life similar to that for

pre-corroded specimens. It is again suggested that the reduction in fatigue life again suggests an interaction between the corrosive fluids and the fatigue crack tip.

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