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ELASTIC AND PLASTIC STRAINS AND THE
STRESS CORROSION CRACKING OF
AUSTENITIC STAINLESS STEELS

Final Report

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ABSTRACT

The influence of elastic (stress) and plastic (cold work) strains on the stress corrosion cracking of a transformable austenitic stainless steel has been studied in several aqueous chloride environments.

Initial polarization behavior was active for all deformation conditions as well as for the annealed state. Visual observation, potential-time, and current-time curves indicated the development of a pseudo-passive (flawed) film leading to localized corrosion, occluded cells and SCC.

SCC did not initiate during active corrosion regardless of the state of strain unless severe low temperature deformation produced a high percentage of martensite. Both elastic and plastic deformation increased the sensitivity to SCC when examined on the basis of percent yield strength.

The corrosion potential, the critical cracking potential, and the potential at which the current changes from anodic to cathodic were essentially unaffected by deformation. It is apparent that the basic electrochemical parameters are independent of the bulk properties of the alloy and totally controlled by surface phenomena.

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INTRODUCTION

The SCC of austenitic stainless steels in aqueous chloride environments has been studied for well over thirty years. Many concepts have been formulated with regard to the examination of the phenomena, some of which have been developed theoretically and others from more practical considerations. For the sake of brevity and in conjunction with the emphasis of this study on the effect of deformation on SCC, it may be helpful to divide our treatment into several interrelated categories: (a) passivity and film nature; (b) mechanisms for SCC; (c) the effect of deformation; and (d) environmental considerations.

A. PASSIVITY AND FILM NATURE

Stainless steels enjoy extensive use in applications where respectable mechanical properties are required in corrosive environments too aggressive for conventional structural materials. The protective character of stainless steels is attributed to the formation of stable, compact, non-porous, regenerative, (i.e. passive) films. The nature of passivity is an area of controversy ⁽¹⁾, although extensive work has been performed

since Faraday ⁽²⁾ formulated a general description of the phenomenon more than a hundred years ago. The difficulty arises because of the simultaneous existence of both chemisorbed structures and three-dimensional oxide structures on many passivated metals and alloys, either of which have been proposed as the passivating agents.

The classical interfacial oxide hypothesis championed by Evans ⁽³⁾ and developed by Akimov ^(4,5), Bonhoeffer ^(5,6) and others, states simply that the oxide films form and display marked resistance to corrosion in aggressive chemical environments. However, the electrochemical behavior of passivated metals and alloys often resembles that observed on platinum rendered passive to hydrogen ionization reactions due to oxygen chemisorption ⁽⁷⁾. In addition, chemisorption of oxygen and oxygen containing species always occur on passivating materials. For these and other reasons a second school has developed a concept attributing passivity to chemisorbed oxygen ⁽⁷⁻⁹⁾.

In order to accomodate all of the experimental observations several investigators compromise film and adsorption theories in an effort to comprehensively explain passivity ^(10,11). Hackerman proposes that adsorbed layers of oxygen can readily explain most of the transient large potential

changes associated with the onset of passivity, and that long lived passivity is probably associated with oxide films of an impermeable and slowly soluble character. It is generally accepted that the very thin passive, and the thicker less protective films, which form under anodic conditions, form via mechanisms elucidated by the Mott-Cabrera Theory (1,12, 13,14). The theory generally applies to film formation at relatively low temperatures ($<300^{\circ}\text{C}$) where mass transport through the film is regulated by electric fields developed as a result of substantial potential gradients. This is in contrast to higher temperature scale formation where ion migration is controlled by chemical gradients in the oxides.

For most anodic films, and in particular passive systems such as stainless steels, metallic ions transfer into and migrate through the film under conditions of constant potential. The potential is developed by the presence of ionized oxygen species either on the surface or throughout the film as well as on the surface. Although the rate controlling step may occur at the interface or in the film, it is generally believed that metal incorporation into the film is kinetically the slowest and irreversible. These conditions result in logarithmic film growth which is observed both on iron (15) and on stainless steels (16,17).

Several analyses have been made on the composition, structure, mechanisms of formation and properties of anodic films which form on austenitic stainless steels in chloride or acid chloride media. The compositions of these films have been examined in passivating acids, acids containing chloride ions, and chloride salt solutions. The significant enrichment of Cr is probably the most striking result. In H_2SO_4 solutions large amounts of Cr are developed in the film with Fe and Ni depletion (18-20).

Other species, such as Cl, Si or S, contained in the alloy in small amounts or present in the environment, often become incorporated in the film in appreciable amounts. In $MgCl_2$ environments, Cr enrichment and Fe and Ni depletion are also observed. Similarly, Cl and Mg obtained from the solution and Si from the alloy, show up in the film in considerable quantities (21,22). These protective films all contain appreciable amounts of oxygen (22-24), hydroxides (25), and water (20,26,27,28), which in conjunction with Cr are the primary passivating agents. One investigation in $MgCl_2$ showed marked Cr enrichment and Fe and Ni depletion, but only inside of pits or trenches, with only small variations observed on the uncorroded surface (29).

The structure of films which form on austenitic stainless steels in these environments is not well established. Some investigators propose the film is an amorphous arrangement of metal, oxygen, hydroxides and chloride complexes (30,31) while others identify the films as oxides (32), spinel oxides (33), or chromium and iron oxy-hydroxides possessing semi-crystalline characteristics (25,34). On the basis of observed oscillations in the optical parameters measured with ellipsometry, Smialowska (19) suggests that the films are mixtures of salts and hydroxide compounds with oxides. The identification of salt films at the bottom of pits (35) is of interest in that it not only shows the dependence of film composition and structure on environment (i.e. solution variations in the pit) it also demonstrates the role the film plays in localized attack.

This is a highly significant observation and introduces the role of the chloride ion in localized attack. Film thickness, is a function of applied potential, alloy composition, solution composition and concentration, and is often related to observed protective capability (20,36). Bednar proposed that the increased susceptibility to SCC that accompanies chloride concentration increases may arise from enhanced film stability (32). It is generally accepted that passivity

is enhanced the thinner the film. Hackerman has developed a detailed model in which film formation is diagrammed in steps delineated successively from oxygen adsorption and ionization to metal migration and oxide formation (37). It is concluded that decreased protective capability with increased film thickness follows directly from this model.

B. PROPOSED MECHANISMS FOR SCC OF AUSTENITIC STAINLESS STEELS

There are a number of comprehensive reviews of the important aspects of the SCC of austenitic stainless steels in chloride containing environments (38-42). A rather brief summary may be helpful at this point.

It is almost universally accepted that the damaging species ultimately responsible for the initiation of localized corrosion processes and the SCC of austenitic stainless steels is the halide (usually chloride) ion (40,41). Its specific adsorption and complexing capability which lead to deterioration of the film as well as increased metal dissolution are the reasons for its detrimental influence (26). Although much study has been directed towards an attempt to more completely understand how chloride ions actually induce localized attack, the nucleation processes still remain elusive (43,44).

Although it is generally agreed upon that chloride interacts with the metal or oxide producing conditions that result in localized corrosion processes which in turn may develop into SCC, there is no general agreement on the role that it plays in the actual initiation and propagation of the crack. The literature is full of imaginative theories describing the mechanism of chloride SCC. They can be classified according to three characteristic models; the electrochemical dissolution concepts, the hydrogen embrittlement models, and the chloride adsorption theory. The following will identify the major theories.

I. ELECTROCHEMICAL DISSOLUTION MODELS

1. Mechano-Chemical, Slip Dissolution (45-48)

Attributes SCC to the dissolution of dynamically straining anodic regions.

2. Film-Rupture (49-54)

This model suggests that slip processes crack the relatively thin films resulting in intensive localized corrosion.

3a. Strain Assisted Precipitation of Anodic Phases (55,56)

The strained austenite transforms to a highly anodic martensite phase which corrodes rapidly.

3b. Hydrogen Assisted Precipitation of Anodic Phases (57,58)

Hydrogen absorbed from the environment induces transformations to martensite which corrode rapidly.

4. Electrochemical Cell Model (49,52,53,59,60)

Based upon the protective capability of the passive oxide film which forms on the crack walls and based on the pH decrease and chloride increases which occur in localized corrosion zones, a continuous dissolution of the crack tip is proposed.

II. HYDROGEN EMBRITTLEMENT MODELS

1a. Classical Hydrogen Embrittlement (61-63)

It is proposed that absorbed hydrogen deleteriously interacts with the metal lattice (either FCC or BCC) and results in brittle fracture at stresses substantially below the yield

strength in normally ductile materials.

1b. Classical Hydrogen Embrittlement of Transformed Ferritic Phases (55,56,58)

It is proposed that austenitic stainless steels intrinsically are not susceptible to SCC and that either environmental or strain assisted transformation to hydrogen embrittled martensitic phases is a necessary precursor to brittle fracture resulting in SCC.

III. CHLORIDE ADSORPTION THEORY (38,64)

1. Proposes that already strained metal bonds are further weakened through adsorption of chloride ions. Mechanism based upon modified Griffith criterion in which strain energy of metal is equated to the surface energy of the incipient crack area.

The electrochemical school is the most diverse, incorporating almost every conceivable dissolution model. Dissolution models appear credible in view of the fact that SCC occurs under conditions which favor localized attack. Furthermore, under cathodic polarization conditions, in which corro-

sion processes are suppressed, SCC is inhibited. Strangely enough, the austenitic stainless steels are the only FCC alloys exhibiting this type of behavior. Under localized stress corrosion cracking conditions, extreme environment variations occur in which neutral solutions become acidified, and chloride concentrations increase. The increased hydrogen ion concentration results from hydrolysis and chloride ions build up in order to balance charge considerations in the isolated and changing solution (28,38,40); both of which conditions synergistically accelerate corrosion processes.

Dissolution theories, on the other hand, are hard pressed to explain discontinuous crack propagation and the embrittled and narrow morphology of the cracks (39). In addition, the role of stress in the phenomena is often minimized or even ignored, and difficulty arises in attempting to rationalize the extremely high current densities necessary to explain the observed crack propagation rates.

It is generally accepted that anodic dissolution processes occurring in localized corrosion regions are rate controlled by the hydrogen reduction reaction. Furthermore, the high anodic currents in pits, crevices, and cracks must be accompanied by an equal cathodic reaction. The primary cathodic

species available for reduction will be hydrogen ions produced by hydrolysis reactions. It is now fairly well established that conditions are optimum for hydrogen reduction in pits and cracks (58,65-68). Several investigations have measured the pH values of isolated solutions from pits and cracks and observed marked acidification to pH values between 1 to 2 (21,69-72). Furthermore, hydrogen has been observed copiously emerging from any region electrochemically equivalent to a pit (39,46,57,65,73,74).

It is this ubiquitous presence of hydrogen which in part provides credibility for explaining the phenomena of SCC of austenitic stainless steels in chloride media as a hydrogen embrittlement process. This model readily explains the discontinuous crack propagation and the narrow and brittle morphology of cracking. Although several face-centered cubic metals and alloys, as well as austenitic stainless steels, are capable of being embrittled by hydrogen concentrations two orders of magnitude higher than those necessary to embrittle body-centered cubic materials ⁽⁶¹⁾, and although hydrogen permeation has been observed under anodic conditions ⁽⁷⁵⁾, the absence of cathodic SCC is difficult to explain from a hydrogen embrittlement standpoint.

It is quite reasonable to speculate that in spite of the apparent resistance of austenitic stainless steels to cathodic induced SCC and their lack of notch sensitivity, the extremely high hydrogen activities ⁽⁵⁸⁾ and modified salt films in regions of local attack can explain the presence of anodic SCC. This concept is supported by the observation that regions around pits have been embrittled by the large amounts of accessible hydrogen ⁽⁷²⁾.

The chloride adsorption model, not as widely accepted, does coherently explain the existence of critical cracking potentials as adsorption potentials. However, the theory does not lend itself to experimental observation ⁽⁴⁰⁾ and ignores the plastic energy term in the modified Griffith equation, leading to a poor theoretical basis for the model.

The significance of a critical cracking potential (E_{cc}) must be considered by the Electrochemical Dissolution and Hydrogen Embrittlement Theories. Uhlig, et al, ^(76,77) recognized that pitting initiation can occur only at potentials more noble than the critical pitting potential (E_p). However, the critical potential for initiation (E_{pn}) is not necessarily the critical growth potential (E_{pg}) which may be substantially more active ^(78,79,80). This critical growth potential is often referred

to as the repassivation potential (E_{rp}) ⁽⁸¹⁾.

One investigation ⁽⁸²⁾ equates the critical crevice potential (E_c) and E_{cc} and proposed that E_{pg} is more noble due to the less occluded nature of pits. The most interesting conclusion is that the critical potential for growth of occluded cells, whether they be for pits, crevices, or cracks are determined primarily by the degree of occlusion, (which ultimately determines the hydrogen ion concentrations in the cells) and by the minimum potential where the current flow is sufficient for establishing a critical chloride concentration in the occlusion ⁽⁸³⁾. It has been further observed that the E_{pn} is more sensitive to environmental perturbations than E_{pg} due to the fact that nucleation is sensitive to bulk conditions, whereas growth is determined by the solution in the occluded cells which often, due to its isolation, approaches a standard condition independent of bulk variations ⁽⁸²⁾.

Pourbaix ⁽⁸⁰⁾ identifies the critical potential as the external potential where an internal potential is developed in pits such that the metal dissolves. Protection occurs when the pits are inactivated by adjusting the external potential to a more negative value than the electrode potential inside the pits. Therefore, cathodic protection against pitting is caused by the suppression of the acidification processes inside of

the pits.

This occluded solution dissolution model for the critical potentials is not the only explanation other than Uhlig's adsorption potential. Repassivation may be determined by the ability of a protective film to form in the occluded cell thus inhibiting further activated dissolution. The work of Baker et al (33), demonstrated that film formation is dependent upon solution specificity, where pH is an important factor.

This summary is by no means comprehensive, but it will help to provide some background for considering the effect of deformation.

C. THE EFFECT OF DEFORMATION

Because of the close relation of pitting to SCC, it is instructive to examine the influence of deformation on pitting. The literature seems to indicate that the breakdown potential (E_b) is independent of deformation although the number of pits increases (84-87). In view of the large quantities of dislocation arrays that are produced during deformation, (not to mention the possible phase transformations which may occur) it is reasonable to associate the increased number of pits with the increase

in number of potential nucleation sites for SCC.

A comprehensive review of the effect of deformation on SCC has been presented by Latanision and Staehle ⁽⁴⁰⁾. This review and more recent studies indicate that sensitivity to SCC increases with increased deformation. However, this is by no means a unanimous opinion, and is further complicated by a lack of consensus upon a normalized criteria of comparison. One of the earliest examinations of the effect of deformation on the SCC of austenitic stainless steels tested cold drawn tubing in U-bend specimens in a 60% hydrated, acidified $MgCl_2$ solution which boiled at $154^{\circ}C$ ⁽⁸⁸⁾. Results indicated that small amounts of deformation increased SCC sensitivity whereas large amounts of drawing, promoting extensive transformation to martensite, were less detrimental. Other work on cold rolled as well as drawn 18-8 stainless in $MgCl_2$ also demonstrated increased sensitivity with deformation ⁽⁸⁹⁾. This analysis was performed on the basis of time to fail versus load as a function of the percent yield strength. In this connection, it must be appreciated that deformation in these steels may raise the yield strength by a factor of 3 or 4.

If comparison is made on the basis of applied stress, the cold worked conditions require longer times to fail because

loads are a smaller fraction of the yield strength. This observation demonstrates the importance of the relation of the applied stress to the yield stress in SCC. From an engineering point of view, comparison on the basis of percent yield strength is more indicative of a materials performance since the yield strength is the primary design criterion.

One of the first studies of primary electrochemical parameters as a function of deformation was performed by Hines and Hoar (90,91). In this work it was determined that SCC sensitivity increases with deformation, and that the open circuit potential (E_{oc}) is increased in the noble direction with time due to film formation whether the specimen is under stress or not. In addition, under stress the E_{oc} displayed a slight active shift just prior to failure which was identified as the initiation of SCC. The increased sensitivity to SCC was attributed to the presence of "quasi-martensite" (92), a proposal earlier presented by Edelenau (55,56) and Rocha (93). However, stable 310 alloys are susceptible to both hydrogen embrittlement and SCC although no accompanying martensite transformation occurs under similar test conditions (61,94). It also has been proposed that martensite formation may explain the increased crack branching that has been observed in deformed specimens (92). However, there are other investigations which indicate

that cracks do not necessarily advance along martensite platelets but that crack growth may actually be impeded by platelets (48).

A systematic examination of the E_{oc} as a function of deformation in $MgCl_2$ (95) indicated the presence of a slight active shift in E_{oc} with deformation (the shift was 30mV for 5% or more prestrain). The investigators interpreted the results to indicate that prior deformation has marked effects on SCC susceptibility. On the other hand, one investigation indicated that regions deformed during corrosion were more easily attacked than previously deformed structures (57).

Other investigations in $MgCl_2$ showed that deformation of up to 30% in a 309 alloy increased sensitivity to SCC (96). This conclusion was made on the basis of percent of yield strength. Elsewhere, it was observed that a maximum sensitivity to SCC occurred at 10% deformation and improved resistance occurred at 30% (97). Here, the data were presented on the basis of applied stress. However, when all the data is examined on the same basis of applied stress, both investigations showed increased sensitivity with deformation. This epitomizes the problems in trying to analyze the influence of deformation on SCC from data in the literature.

Indications of a minimum in resistance to SCC at around 10% deformation were also observed in a stable 310 alloy ⁽⁹⁸⁾ and in a 316 stainless steel ⁽⁹⁹⁾. In both of these as well as other investigations, wire specimens were examined. There are indications that one should be concerned over the utilization of small cross section specimens in an analysis of SCC due to the fact that pitting and corrosion may further reduce the cross section until simple tearing occurs and SCC is not involved at all.

Another basis for comparing relative sensitivities to SCC requires the determination of threshold stresses. Some of the earlier work performed by Logan et al, ^(49,50) in a .5N NaCl, .1N Na₂NO₃ solution exhibited a monotonic increase in threshold stress with deformation for a 301 alloy, and a 304 alloy showed a similar increase of threshold stress for deformations up to 26% followed by a decrease at 35%. A similar profile to that observed with 304 was obtained in a .5% titanium stabilized 321 alloy.

Although the literature contains many references which propose that threshold stresses actually exist, SCC has been produced at very low applied stresses, even approaching conditions of zero applied load ^(48,95,99-101). It has been proposed

that substantial stresses can exist residually or be induced by expanding, constrained corrosion products.

A major investigation of the influence of deformation on the SCC of austenitic stainless steels in environments other than MgCl_2 was conducted by Phelps and Mears ⁽¹⁰²⁾. In MgCl_2 , 302 and 304 alloys displayed initial decreases in resistance to SCC followed by improvement at 50% cold reduction. No failures occurred in neutral NaCl solutions within 1000 hours of immersion. However, with H_2S additions cold rolled structures were susceptible in a 3% NaCl environment. The less stable 302 alloy displayed a greater sensitivity when cold rolled than the 304 alloy. The cold rolled 302 alloy containing α martensite displayed both anodic and cathodic failure branches characteristic of classical hydrogen cracking. Uhlig et al ⁽¹⁰³⁾ examined the effect of deformation and martensite on the SCC behavior of an 18-8 alloy in MgCl_2 . Specimens plastically strained at -196°C producing substantial amounts of deformation martensite were immune to cracking.

A previous analysis by the present authors was conducted on the effect of deformation on failure times and the primary electrochemical potentials ⁽¹⁰⁴⁾. In this analysis a stable 310 and a transformable 301 alloy were examined in MgCl_2 in

order to independently examine the effect of deformation and martensite. The results indicated that failure times shortened with deformation whether martensite was present or not. The open circuit potentials were approximately -330 to -340 for 310 and -380 to -390mV for 301. In addition, the critical cracking potentials (E_{cc}) were between -345mV and -360mV for the 310 alloy and between -375mV and -385mV for the 301 alloy for all deformation conditions. It is significant to note that these values were identical with the potential where the current changed from anodic to cathodic for each respective alloy and approximately equal to the steady state E_{oc} .

Uhlig (105) determined that $E_{cc} = -350\text{mV}$ for a 310 alloy. Uhlig et al (105,106) and Smialowski and Rychcik (107) determined E_{cc} to be -385mV for an 18-8 alloy. Barnartt and Van Rooyen (74) reported a slightly more active E_{cc} at -410mV for an 18-8 alloy. The E_{cc} for a 304 alloy in aerated, saturated NaCl at 107°C was also determined to be -410mV by our previous investigation although open circuit failure times were so long (> 1000 hrs) that unmodified NaCl environments were not considered practical for conducting laboratory examinations. The absence of significant variations in the primary electrochemical parameters in the MgCl_2 solution prompted concern as to whether this environment was too aggressive and masking some of the

effects. In addition, MgCl_2 is not extensively encountered and not as interesting as NaCl .

D. Environmental Considerations

Many environments containing chloride ions (other than MgCl_2) induce SCC in austenitic stainless steels and are therefore candidates for the examination of the influence of deformation. Extensive basic SCC analyses have been performed in H_2SO_4 with and without NaCl additions. In 1, 5, or 10N H_2SO_4 solutions containing more than .01M NaCl , SCC occurs in the active region (108-111). When NaCl additions to these highly acid solutions are small, less than approximately .5M, E_b is relatively constant and only with substantial NaCl additions will breakdown occur at more active potentials (110,112).

The observations of active state SCC and the absence of SCC at E_b prompts one to inquire whether there exists a critical difference in the nature of the respective films and whether localized attack leading to SCC in the active region can be described as the breakdown of a truly passive film or as the normal behavior of an intrinsically flawed "pseudo-passive" film. This is a critical consideration which will be developed further.

HCl is another environment capable of producing active state SCC when the concentration is between .5 and 3M (113,114). However, these highly acidic environments appear too aggressive for present purposes. On the other hand, pH modifications of salt solutions may prove promising in providing an optimum environment for examining various electrochemical or metallurgical SCC parameters, such as the effect of deformation. Film formation is extremely pH sensitive as stated before (33) and as indicated in recent work. At a pH = 0 only active corrosion occurred. However, at pH = 1 a protective, thick film developed and the polarization curve displayed a low current region of potential (115). SCC sensitivity has been shown to increase as a function of chloride concentration in MgCl_2 (55,101), NaCl (55,116,117), and LiCl (32,89,101). However, it is not clear whether this variation is due to chloride concentration or changing boiling temperatures (118).

The variations in sensitivity to SCC that occur between different cation species which comprise the salts are often as dramatic as concentration effects (116,119). Largely, these variations have been attributed to the changes in pH resulting from hydrolysis (28,58,120-123). However, it has been demonstrated that the cation effect persists after pH normalizing adjustments are made (119). Therefore, Rhodes (58) cogently

argues that the activity of hydrogen is the important factor. The activity coefficients of hydrogen (γ_{H^+}) in concentrated boiling salt solutions are not known although the ratio of γ_{H^+} in $MgCl_2$ and $LiCl$ have been calculated by Rhodes from the values of the standard H^+/H_2 couple (E_H°) and suggests that γ_{H^+} is greater in $MgCl_2$ than in $LiCl$ and increases with concentration.

The importance of hydrogen ions in the phenomena of SCC is central to both the electrochemical dissolution theory of SCC and the hydrogen embrittlement model. This assertion is easily understood for the latter case, but requires explanation for the former. Some work indicates that the presence of oxygen is important as a reducible species and therefore affects SCC processes (123-125). On the other hand, Barnartt and Van Rooyen (74) and Uhlig and Lincoln (126) determined that aeration and deaeration had no effect on potential time curves or on cracking times in $MgCl_2$.

The assumption that increased hydrogen ion activity results in increased corrosion rates and in increased cracking if the corrosion reactions are limited to localized regions is supported by the observation that Cl adsorption (127-132), as well as heavy metal ion additions (120,127,133,134) inhibit the hydrogen

reduction reaction in acid and chloride environments thus reducing general corrosion and SCC sensitivity. Although it is substantiated that the cathodic inhibition due to the chloride ion is a result of specific adsorption, it is not clear whether heavy metal ions inhibit via underpotential deposition (127) or the formation of an insoluble lead sulfide film (134). In view of the fact that increased hydrogen activity increases SCC sensitivity, it is understandable that some investigators have observed that acid additions in salt solutions enhance SCC (74, (119,120,129,135,136)).

There have been suggestions in the literature that in concentrated chloride environments the primary passive film is drastically modified in regions of acidification. It is not clear whether this film is an oxide (33) or a salt layer (19), however, it is clear that the film is extremely susceptible to localized corrosion leading to SCC. Podabaev (120) and Baker et al (33) demonstrate that acidification either in pits or by bulk solution modifications result in thickening of the film and in structural and compositional variations, which they identify as the critical factors in SCC initiation. This critical role of the secondary film is generally interpreted by proponents of the dissolution models as inhibiting lateral dissolution thus enhancing SCC (40).

The hydrogen embrittlement model also relegates an important role to the film as a precursor to establishing electrochemical conditions conducive to localized corrosion which in turn results in increased hydrogen activities in the solution leading to intense local hydrogen absorption. These localized corrosion processes occur after film breakdown occurs or by the active dissolution of preexistent flaws (1,3,137-139). Others suggest that for initiation of SCC there must exist a coincidence between the location of some kind of defect in the film and in the metal surface (137,140). It is important to note that the invisible, highly protective films which form in $MgCl_2$ and $LiCl$ solutions are intrinsically flawed.

MATERIALS AND PROCEDURES

The primary alloy examined was a transformable 301 austenitic stainless steel of commercial grade received in the annealed condition. A standard commercial 304 alloy was examined for comparison. Compositions, yield strength, and the amount of martensite present are given in Table 1-3. The yield strength of the 301 alloy in various deformed conditions is presented in Figure 1. The yield strengths versus deformation by rolling performed at different temperatures is in excellent general agreement with the results of Krivobock and Talbot (142).

Yield strengths were determined from at least two stress strain curves utilizing a mechanical extensometer. For martensite contents up to approximately 20%, a magnetic indicator was used for determinations. For additional verification Debye Scherrer X-Ray diffraction patterns were obtained in order to identify whether the martensite was α or ϵ and to provide qualitative indications of the amount of transformation. In order to enhance transformation to both α and ϵ martensite, specimens were precooled to -196°C and then rolled ⁽¹⁴¹⁾. To compare the influence of a given amount of deformation with and without transformation, specimens were deformed above the M_d temperature.

The design and selection of the final test environment was based on the results of the earlier stages of this investigation where MgCl_2 and 3% NaCl solutions were employed as well as on a consideration of the influence of pH as indicated in the literature (see Introduction). The primary environment contained HCl acidified NaCl solutions with film stabilizing additions such as Na_2SO_4 . This particular combination had the advantage of not introducing any extraneous ions. Reagent grade chemicals and double distilled H_2O was used. Deaeration was accomplished by bubbling N_2 and aeration by bubbling either air or oxygen.

Specimen strips were ground on a tensile grinding machine to a reduced section specimen resulting in better reproducibility than wires (107). Specimen preparation involved sanding through 600 grit silicon carbide paper, cleaning in Alconox soap and rinsing in distilled water prior to immersion. Tensile loading was applied using the standard lever apparatus shown in Figure 3. Loading levels for open circuit SCC tests were either 70% or 95% of the yield strength. All E_a SCC tests were conducted at 70% of the yield strength.

Potentials were recorded using either an electrometer or a potentiostat in conjunction with strip chart recorders. For applied potential SCC tests, potentiostats were used to control the potential with platinum as an auxiliary electrode. Currents were then recorded as functions of time using strip chart recorders. Failure times were determined using switch activated clocks. All potentials were measured relative to the standard saturated KCl calomel electrode (SCE). A potentiodynamic analyzer was used to generate potentiodynamic polarization curves (potential versus current). A 500 mV/hour sweep rate was used, unless otherwise noted, and all curves are normalized in terms of current density (amps/cm^2). The polarization cell is shown in Figure 4.

Specimens were examined with light microscopy in order to determine if SCC had occurred and whether cracks were associated with microstructural defects or martensite phases. Electroetching was conducted at +6V in an oxalic acid solution for 30 to 60 seconds. Scanning Electron Microscopy (SEM) was utilized to examine fracture surfaces and identify whether cracking was trans- or inter- crystalline. The compositions of films were determined with energy dispersive x-ray analysis.

RESULTS AND DISCUSSION

This investigation involves: (1) the design and characterization of an acidified sulfate containing NaCl environment; (2) the utilization of this environment in the examination of the effect of deformation on SCC; and (3) the analysis of film composition. the various electrochemical and metallurgical parameters of significance are:

- E_{oc} - Open Circuit Potential (Corrosion Potential)
- E_{cc} - Critical Cracking Potential
- E_b - Breakdown Potential (The Classical Breakdown of a Truly Passive Film)
- E_{+-} - Potential where steady state current shifts from anodic to cathodic.
- E_a - Applied Control Potential

- E_{pn} - Critical Pit Nucleation Potential
- E_{pg}, E_{rp} - Critical Pit Growth or Repassivation Potential
- E_c - Critical Crevice Potential
- E_{oc} - Versus Time
- Current Versus Time
- Failure Time; Open Circuit
- Failure Time; Applied Potential
- M_d - Critical Temperature for Deformation Martensite.

Section 1. Environment Design and Characterization

Initial examinations were conducted in solutions at room temperature previously employed by Uhlig and Leckie⁽⁷⁶⁾ where it was demonstrated that sulfate stabilized the film. Table 4 shows that SCC did not occur at room temperature in these acidified, low NaCl environments under open circuit conditions or under E_a conditions near E_b . No attack occurred at open circuit and failures at E_b resulted from either crevice or general corrosion.

SCC does not occur in these low NaCl environments even at elevated temperatures. Figures 5 through 9 present typical polarization curves for .1M and .5M NaCl solutions. It is clear

that the sulfate enhances film formation and that acidification results in the appearance of an active branch. Table 7 shows that SCC does not occur in short times in these acidified, low NaCl environments. When attack does occur under applied potentials, it is either pitting or crevice corrosion.

In view of the inability to obtain SCC in reasonable times in low NaCl environments, a systematic examination of solutions with increased chloride was conducted. Figures 11 through 20 indicate that even in concentrated acidified solutions the sulfate influences film stability. On the other hand, increased chloride content and acidification destabilize the film and activate the surface. It is important to note that although chloride and acidification activate the specimen, film development eventually occurs due to the precipitation of insoluble corrosion products. This film development is characterized by a shift in E_{oc} from around -450 to -370. Increased chloride content and acidification reduce the time for this shift.

Polarization behavior may be quite different after the shift in E_{oc} occurs, as demonstrated in Figures 21 through 23. Although the polarization curve appears active, the specimen is filmed and is in a semi-protective or pseudo-passive state.

The increase in current with increased polarization indicates that the somewhat thick green film is involved in localized breakdown. This demonstrates the enigmatic nature of polarization data for conditions undergoing localized electrochemical processes. Only net currents are monitored as a function of potential and therefore visual observation or other electrochemical analyses must supplement the polarization data. SCC was not observed in less than 100 hours unless the NaCl concentration was near 1.8M and acid additions were 5 ml/lt. SCC data for higher NaCl environments are presented in Tables 6, 7, and 8.

Increased chloride and acidification resulting from crevice corrosion or bulk solution modifications further enhance SCC. This increased sensitivity to SCC is related to the development of the semi-protective (i.e. pseudo-passive) film and is characterized by the rapid shift in the E_{oc} to -370 mV. When unacidified, the E_{oc} remains active at -450 mV for at least 400 hours in a concentrated NaCl solution. Only a thin invisible film forms which is more resistant to localized attack.

The protective nature of the film is clearly indicated by the shift in E_{oc} under open circuit conditions (shown in Fig. 24) and by the decrease in current at $E_a = -250$ (see Fig. 25).

These transients both result from a "transformation" in the film which is not presently identified. Increased activation caused excessive pitting and corrosion at $E_a = -200$, thus overriding or masking the development of SCC, (see Fig. 26). Similar behavior is observed when the chloride content is increased.

An examination of Table 9 and Figs. 27 through 31 demonstrate that the development of the film causing the shift in E_{oc} results from acidification. Specifically, Figures 27, 28 and 29 indicate that the time for the shift in E_{oc} is a function of sulfate content, and temperature. Figures 30 and 31 show that aeration and the application of stress (elastic deformation) have no observable effect on the E_{oc} - time profile. This absence of an influence of oxygenation on the E_{oc} - time profile further supports the consensus that the primary cathodic reaction in these boiling concentrated salt solutions is the reduction of hydrogen ions.

The independence of the time of loading on the time to fail at the upper plateau (see Figure 31) indicates that the initial anodic transient does not directly contribute to the SCC processes. When the load is applied after the E_{oc} shift the time to fail is 20 hours. This is approximately equal to the time under load before failure at the upper plateau even

when loading is applied 10 hours before the E_{oc} shift. Therefore, it is most significant to note that SCC does not initiate in this environment during active corrosion.

The preceeding results provide sufficient information for selecting an adequate NaCl environment for the more detailed examination of the effect of elastic and plastic deformation on the SCC of austenitic stainless steels and to allow sufficient data to be accumulated in a reasonable length of time. Therefore, a deaerated, 4.9M NaCl, .15M Na_2SO_4 , boiling solution, acidified with 3 ml HCl/lit. was selected as the primary environment for the study of the effects of deformation on the stress corrosion cracking of austenitic stainless steels. In order to demonstrate that this environment is a generic SCC agency, an O.C. SCC test was conducted on an extensively researched 304 type alloy, (see Figure 32). SCC still occurred and the E_{oc} 's were approximately the same.

Section 2. THE EFFECTS OF DEFORMATION

The initial polarization behavior is independent of deformation. Polarization curves for the various conditions of deformation as well as for the annealed alloy are typified

by the curve of Figure 33. The initial E_{oc} was between -430 and -460 and all conditions displayed active control. That active corrosion is occurring is additionally supported by the observation of copious hydrogen evolution and the build-up of corrosion products.

The time for failure under open circuit conditions decreases for room temperature deformations of up to 25% with no further decrease at 50%, (see Table 10 and Figure 34). The E_{oc} values versus time are presented in Figures 35 through 38 for room temperature deformation conditions loaded to 70% of the respective yield strength. All curves show the rapid shift in E_{oc} from the same initial values of $E_{oc} \approx -450$ to the same $E_{oc} \approx -380$, regardless of the amount of deformation and/or the presence of martensite.

Relevant SCC data for below room temperature deformations are presented in Table 11 and Figure 39 and demonstrate that the failure time versus deformation profile is similar to that obtained with room temperature deformation. Just as for deformation at ambient temperature, deformation at -196°C results in E_{oc} versus time curves have identical initial and final E_{oc} 's, and also the same as for the annealed state. The time for the E_{oc} shift decreases with increasing deformation. However, 30%

deformation at +150°C results in an E_{oc} shift in approximately the same time as the annealed condition, (see Table 11). Figure 40 shows that the initial and final E_{oc} 's are also the same as those obtained with the undeformed alloy. Remember that deformation above M_d does not produce martensite. Thus, although the bulk properties of the alloy are widely varied from fully annealed to combinations of deformation and transformation products not to mention substructure and defect variations, the basic electrochemical parameters do not change. Clearly, SCC initiation is totally controlled by surface phenomena.

As expected, loading to higher stress levels (95% of the yield strength) reduced the time for SCC failure. (See Table 12 and Figure 41). On the other hand, application of a higher stress had no influence on the E_{oc} versus time relations, again, regardless of the deformation conditions.

The times to fail when loads are applied after the shift in E_{oc} are approximately the same as the time under load at the more noble E_{oc} for specimens loaded after only one hour in the environment, (See Table 13). Figures 34, 42 and 43 show this is the case for the annealed condition and Figures 44-46, compared with Figures 36 and 37, demonstrate it is also true for deformed specimens.

The observation that the time to failure is approximately 20 hours for the annealed condition whether the load is applied after 12 or 22 hours demonstrates that the general SCC processes occurring in the film are initiated after the stress is applied, (compare Figures 42 and 43) quite consistent with the fact that SCC requires the simultaneous application of stress and environment. Therefore, there is no influence of "ageing" of the film at the quasi-protective E_{oc} on SCC. The stress must be applied in order to initiate the electrochemical and metallurgical processes associated with SCC.

The general conclusion of the O.C. SCC data is that increased deformation results in increased sensitivity to SCC when comparison is on the basis of a fixed percentage of the yield strength. Sensitivity is increased with deformation whether or not transformation to martensite occurs. The low temperature deformation conditions appear to be most severe. However, there are parallel increases of both martensite content and yield strengths with low temperature deformation making it difficult to identify which factor causes this increased sensitivity to SCC.

The third stage in the analysis of the effect of deformation involved the determination of the critical cracking

potential (E_{cc}). Table 14 lists E_a SCC data and Figures 47-50 present some of the typical current versus time curves obtained from the many applied potential SCC tests for various deformation conditions. The current time profiles for all deformation conditions are similar in form and characterized by an initial high anodic current transient, followed by a decay in the current to the steady state value associated with the specific E_a . The initial currents are anodic for all E_a values more noble than -450 mV although steady state currents are cathodic only for E_a 's more active than -380 mV.

For room temperature deformations up to 25%, there are no significant effects on the E_{cc} or on the potential at which the current reverses (E_{+}). Table 15 and Figures 51-53 show that the E_{cc} and the E_{+} for these ambient temperature deformations lie between -375 and -385 mV.* For deformations of 25% at -196°C and for the 30% deformation at -150°C, premature failures occurred when loading was performed at one hour immersions. The initial anodic transient and high stress levels resulted in excessive reduction in the cross sections and tearing. Therefore, for these conditions, loading was conducted after the potential shift in order to suppress the initial high

* Each data point on Figures 51 through 58 represent the determination of a complete current-time to fail curve at a fixed applied potential as typified by Figure 47.

anodic transient.

The 30% deformation condition (containing no martensite) displayed E_{cc} 's (see Figure 54) and E_{+} values similar to those obtained in the annealed condition. The E_{+} 's for the 25% low temperature deformed condition and the 50% room temperature condition were also approximately the same as that for the annealed alloy. However, for these latter two conditions cracking occurred at E_a 's much more active than E_{+} 's. (See Figures 55 and 56). Both of these conditions are extensively transformed to martensite (BCC) and display ultra high yield strengths, which lead to cathodic cracking. For the 25% low temperature deformation condition, the failures at $E_a = -420$, -450 and -475 all occurred under cathodic currents.

When a 50% room temperature rolled specimen was loaded at $E_a = -450$ mV the current initially was anodic and eventually shifted cathodic. Although failure occurred at this very active potential, it was not certain whether the failure resulted from local anodic dissolution initiated during the anodic transient, or whether the failure was caused by classical cathodic charging. Therefore, a duplicate test was conducted except that the load was applied after the shift in E_{oc} . Under this condition the current is primarily cathodic. These results

strongly indicate that the failure is a result of the embrittlement of the BCC martensite phases due to hydrogen. All of the E_a SCC tests discussed to this point were conducted at stress levels of 70% of the yield strength.

For the 11% low temperature deformation condition, two loading procedures were followed. Specimens were loaded after one hour and after 20 hours to 70% of the yield strength. The E_{cc} for the 1 hour loading procedure was -385 mV (Fig. 57) and for the latter E_{cc} was -410 mV, (Figure 58). Unlike the more highly deformed 25% condition, no failures occurred active to E_{cc} for the 11% deformation condition.

It may be concluded from the applied potential SCC data that:

1. The E_{+} is independent of the amount of elastic or plastic deformation and other structural variations resulting from deformation.
2. When deformation produces high strength levels and large amounts of transformation to BCC martensite, cathodic cracks develop.
3. The E_{cc} is relatively insensitive to deformation.

The close proximity of the E_{cc} to the E_{+} indicates that SCC occurs in this environment under the same electrochemical conditions as localized corrosion. In other words, the E_{cc} is identical to the E_{rp} . Although proponents of dissolution theories would argue that this strongly supports their model, it must be recognized that the corresponding presence of hydrogen ions under these electrochemical conditions provides equal phenomenological support to the hydrogen embrittlement theory for SCC.

Metallographic examinations were conducted for all O.C. SCC tests in order to positively determine whether the failures were SCC. Figures 59 and 60 show typical micrographs of etched and unetched specimens demonstrating secondary stress corrosion cracks. Cracking appears to be predominantly transgranular.

Under E_a conditions, it is more difficult to develop and observe secondary stress corrosion cracks. As the E_a is increased in the noble direction from the E_{cc} , pitting corrosion is enhanced. Nevertheless, at or slightly noble to E_{cc} , SCC was definitely observed.

Secondary cracking was more extensive for the annealed and deformation conditions which did not yield a high percentage of martensite. On the other hand, where substantial martensite

was produced, a single crack defined the major extent of SCC. This may be attributed to the higher stress level and to increased notch sensitivity of the BCC phase.

Scanning electron microscopy was conducted on fracture surfaces in order to determine the mode of failure. Under open circuit conditions, corrosion made it impossible to draw any conclusions as to whether the SCC occurred by transgranular or intergranular fracture. Intergranular cracking occurred in specimens which contained substantial amounts of martensite, such as those rolled at liquid nitrogen temperatures. This is apparent in Figure 61.

Section 3. FILM COMPOSITION

The film which forms on annealed 301 was analyzed utilizing energy dispersive x-ray analysis. Figures 62-64 present the count profiles versus energy for an unexposed specimen, a specimen exposed for two hours, and a specimen exposed for 48 hours. The two exposed conditions were selected in order to analyze the film composition before and after the shift in the E_{cc} .

As expected, the profiles indicate the presence of Fe, Cr, Ni, and Si. Figure 63 shows that after only a two hour immersion the relatively thick anodic film is almost completely depleted of Fe and Ni. The film is Cr enriched and contains large amounts of Cl and some S. After the potential shift, (a 48 hour immersion) the film is even more enriched in chromium. The profile in Figure 64 gives no indications of Fe and Ni and the 48 hour film contains less chloride and slightly more sulfur. The sulfur and chloride undoubtedly are obtained from the solution.

In order to analyze the nature of the film, the influence of mechanical abrasion on the E_{oc} was examined. In this experiment the film was allowed to form under open circuit conditions until the E_{oc} shifted from -450 to -380 mV. The specimen was removed and then rubbed quite vigorously with a paper towel until the thick, green, film was apparently removed. The E_{oc} was still -380 after the specimen was reimmersed. This procedure was repeated and again the E_{oc} remained at -380 mV. However, light abrasion with 600 grit silicon carbide paper resulted in a return of the E_{oc} to -450 mV indicating that the protective film had been disrupted or removed.

These results indicate that the thick, anodic film, composed primarily of Cr, Cl and S, may not be the source of protec-

tion to general corrosion observed at the upper potential. The protection quite possibly could be provided either by a chemisorbed layer of oxygen or a thin, invisible oxide film which displays remarkable adherence capability and some resistance to mechanical abuse. Apparently, this film is related to the build-up of corrosion products which may provide insulation from the solution allowing the film to form. The corrosion products may have to achieve critical constituent concentrations for the necessary "transformation" to occur. In any event, this film is not the same as the original normal passive film.

SUMMARY

1. Increased chloride concentration, increased sulfate concentration and acidification enhance the development of SCC in austenitic stainless steels.
2. Initial polarization behavior is active for all deformation conditions as well as for the annealed alloy. Initial exposure to the environment induces general corrosion. The electrochemical processes preceeding the establishment of localized corrosion and SCC do not initiate while the alloy is undergoing general corrosion.
3. Information obtained from polarization behavior is not always sufficient for characterizing the nature of corrosion. Visual observation, potential versus time curves and current versus time curves provide critical information for determining whether the alloy is developing a protective film and undergoing localized corrosion preceeding SCC.
4. A flawed, pseudo-passive film develops from the corrosion products as the result of an unidentified "transformation". The film is highly susceptible to the development of occluded cells. The build-up of chloride and acidification in these cells result in the initiation of SCC.

SUMMARY continued

5. The corrosion products are enriched in Cr, depleted of Fe and Ni and contain Cl and S acquired from the solution.
6. SCC does not initiate during active corrosion regardless of the state of deformation if the alloy does not have substantial amounts (80-90 plus percent) of martensite.
7. When examined on the basis of percent yield strength, both elastic (stress) and plastic (cold work) deformation increase sensitivity to SCC in terms of shortening time to fail.
8. The open circuit potential, the critical cracking potential and the potential where the current changes from anodic to cathodic are essentially unaffected by deformation. These critical potentials lie in the range of repassivation approximately between -380 and -400 mV. SCE. This potential range is conspicuously the same for a number of chloride environments known for their ability to promote SCC. Clearly, the basic electrochemical parameters are independent of the bulk properties and totally controlled by surface phenomena.

SUMMARY continued

9. Light Microscopy indicates that SCC in this environment is primarily transgranular regardless of the state of deformation. Scanning electron microscopy showed that intergranular SCC occurred only under applied potential conditions for specimens cold rolled below room temperature. This intergranular mode of fracture is attributed to the presence of large amounts of martensite making the alloy more sensitive to hydrogen embrittlement. For conditions producing the largest amounts of martensite, cathodic cracking was observed, further indicating that martensite greatly increases the sensitivity of the alloy to hydrogen embrittlement processes.

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Table 1: Chemical Composition (%). 301 Austenitic Stainless Steel.

<u>Cr</u>	<u>Ni</u>	<u>Mo</u>	<u>C</u>	<u>Mn</u>	<u>P</u>	<u>S</u>	<u>Si</u>	<u>Fe</u>
17.95	7.20	.18	.094	1.02	.014	.017	.70	bal.

Table 2: Chemical Composition (%). 304 Austenitic Stainless Steel.

<u>Cr</u>	<u>Ni</u>	<u>Mo</u>	<u>C</u>	<u>Mn</u>	<u>K</u>	<u>S</u>	<u>Si</u>	<u>Cu</u>	<u>Fe</u>
18.32	8.48	.19	.07	1.68	.02	.004	.51	.10	bal.

Table 3: Deformation Temperature, .2% Offset Yield Strength,
% Martensite, Phases Present. 301 Austenitic Stainless Steel.

<u>% Deformation</u>	<u>Deformation Temperature (°C)</u>	<u>Yield Strength (KSI)</u>	<u>% Martensite *</u>	<u>Phases Present #</u>
0	—	46.0	0	γ
15	+20	108.6	12	γ , α Mart.
25	+20	167.6	20+	γ , α Mart.
50	+20	245.0	20+	γ , α Mart.
11	-196	163.5	20+	γ , α & ε Mart.
25	-196	276.5	90+	γ , α & ε Mart.
30	+150	122.4	0	γ

* Determined by Magnetic Indication

Determined by X-Ray Diffraction

TABLE 4

OPEN CIRCUIT (O.C.) AND APPLIED POTENTIAL (E_a) SCC TESTS. ROOM TEMPERATURE. DEAERATED

<u>NaCl</u> <u>(M)</u>	<u>Na₂SO₄</u> <u>(M)</u>	<u>ml</u> <u>HCl/lt</u>	<u>pH</u>	<u>E_{OC}(mv)</u>		<u>E_a</u> <u>(mv)</u>	<u>TTF</u> <u>(hrs)</u>	<u>COMMENTS</u>
				<u>bef.</u>	<u>aft.</u>			
.1	.15	0	6.5	-563	-560	O.C.	N.F. 190	No Attack
.1	.15	1	3.0	-495	-	+675	24	Crevice
.1	.05	1	3.0	-	-	+300	<10	Corrosion
.5	.1	1.5	1.5	-	-	O.C.	N.F. 262	No Attack

TABLE 5

APPLIED POTENTIAL (E_a) SCC TESTS. LOW NaCl. DEAERATED (100°C). LOAD AFTER ONE HOUR IMMERSION

<u>NaCl</u> <u>(M)</u>	<u>Na₂SO₄</u> <u>(M)</u>	<u>ml</u> <u>HCl/lt</u>	<u>pH</u> <u>bef.</u>	<u>aft.</u>	<u>E_{oc}</u> <u>(mv)</u>	<u>E_a</u> <u>(mv)</u>	<u>TTF</u> <u>(hrs)</u>	<u>COMMENTS</u>
.1	.05	3.0	1.6	1.9	-290	-200	NF 300	Pitting
.1	.05	.5	2.5	2.7	-430	-200	NF 124	No Attack
.1	.15	.5	2.9	-	-440	-250	NF 200	No Attack
.1	.15	.5	2.5	5.3	-	- 75	89.5	Crevice
.1	.15	.3	2.9	5.2	-419	+200	1.6	Pitting
.5	.05	3.0	1.4	-	-460	+ 25	.7	Pitting
.5	.15	.5	2.2	4.7	-400	-400	NF 190	No Attack

TABLE 6

OPEN CIRCUIT (O.C.) AND APPLIED POTENTIAL (E_a) SCC TESTS, 1.5M, 1.8 M NaCl. DEAERATED (103°C)

NaCl (M)	Na ₂ SO ₄ (M)	ml HCl/lt	pH		LOAD TIME (hrs)	E_{oc} (mv)		E_a (mv)	TTF (hrs)	COMMENTS
			bef.	aft.		bef.	aft.			
1.5	.05	3	1.4	2.0	29	-430	-333	-350	NF 144	No Attack Current = -2ma
1.5	.05	3	1.4	2.4	45	-446	-314	-300	247	SCC in Crevice Current = +.5ma
1.5	.05	3	1.5	2.3	1	-440	-	-250	NF 262	SCC in Crevice Current = +1.0ma
1.5	.05	3	1.4	1.7	1	-440	-340	O.C.	NF 367	No Attack
1.5	.05	3	1.1	-	72	-440	-343	O.C.	NF 300	No Attack
1.8	.05	5	1.0	3.0	96	-420	-320	-300	81	SCC Current = +.5ma
1.8	.05	5	1.4	2.0	1	-420	-	-250	52	Crevice Current = +7ma
1.8	.05	5	1.0	4.4	1	-420	-	-200	25	Disintegrated Current = +20ma
1.8	.05	5	.9	1.4	1	-420	-345	O.C.	NF 190	SCC
1.8	.05	5	.5	1.1	69	-420	-340	O.C.	NF 407	SCC at Liquid Air Interface

TABLE 7

OPEN CIRCUIT AND APPLIED POTENTIAL SCC TESTS. MEDIUM, HIGH, NaCl. DEAERATED.
LOADED AFTER ONE HOUR IMMERSION. (103°C to 107°C)

<u>NaCl</u> <u>(M)</u>	<u>Na₂SO₄</u> <u>(M)</u>	<u>ml</u> <u>HCl/lt</u>	<u>pH</u>		<u>E_{oc}(mv)</u>		<u>E_a</u> <u>(mv)</u>	<u>TTF</u> <u>(hrs)</u>	<u>COMMENTS</u>
			<u>bef.</u>	<u>aft.</u>	<u>bef.</u>	<u>aft.</u>			
2.0	.05	-	1.5	2.1	-440	-	-280	114	Crevice
2.9	.05	3.0	1.1	-	-441	-350	O.C.	NF 107	No Attack
3.9	.05	.4	1.8	2.0	-470	-300	O.C.	NF 163	Black, Green Film
3.9	.05	1.0	1.3	1.8	-440	-388	O.C.	82.3	SCC
3.9	.05	3.0	.8	1.4	-427	-380	O.C.	65.8	Green Film
3.9	.15	1.5	1.0	-	-400	-300	O.C.	62	SCC
3.9	.15	3.0	.8	1.5	-440	-380	O.C.	44	Green Film
4.9	.15	0	6.1	-	-500	-479	O.C.	NF 240	SCC
4.9	.15	3.0	.8	1.5	-450	-380	O.C.	33.5	Green Film
									SCC
									Green Film

TABLE 8

OPEN CIRCUIT (O.C.) AND APPLIED POTENTIAL (E_a) SCC TESTS
 4.9M NaCl, .15M Na₂SO₄, 3ml HCl/lt. DEAERATED. (107°C). LOAD AFTER ONE HOUR IMMERSION

<u>E_a</u>	pH		E_{oc} (mv)		<u>TTF hrs.</u>	<u>COMMENTS</u>
	<u>bef.</u>	<u>aft.</u>	<u>bef.</u>	<u>aft.</u>		
O.C.	.8	1.5	-450	-380	33.5	SCC
-400	.8	1.2	-440	-	NF 120	No SCC Current Cathodic
-380	.6	1.2	-443	-	NF 170	No SCC Current Cathodic
-360	.5	1.7	-450	-	23.0	SCC Current Anodic
-350	.6	4.5	-450	-	6.3	SCC, Heavily Corroded Current Anodic

TABLE 9

OPEN CIRCUIT (O.C.) SCC TESTS IN 4.9M NaCl. (107°C)
LOADED AFTER ONE HOUR IMMERSION

<u>Na₂SO₄</u>	<u>Aer</u>	<u>ml HCl/1t</u>	<u>pH</u>		<u>E_{OC}(mv)</u>		<u>TIME FOR E_{OC} SHIFT (hrs)</u>	<u>TTF hrs.</u>	<u>COMMENTS</u>
			<u>bef.</u>	<u>aft.</u>	<u>bef.</u>	<u>aft.</u>			
0	A	0	6.0	-	-450	-450	No Shift	NF 170	No Attack
0	D	0	6.0	-	-500	-510	No Shift	NF 170	No Attack
.15	D	0	6.0	-	-500	-479	No Shift	NF 240	No Attack
0	D	3.0	.3	1.4	-420	-375	5.5	20	Loaded After
0	A	2.0	.3	-	-454	-386	-	81.9	25 hrs. SCC
.15	A	2.0	.3	2.4	-466	-366	-	28.4	Pitting, SCC
.15	D	3.0	.8	1.5	-450	-380	11.0	33.5	SCC
.15	D	3.0	.8	1.5	-455	-380	12.2	-	No Stress
.15	A	3.0	.6	1.5	-450	-370	11.5	20.7	SCC
.15	D	3.0	.7	1.3	-430	-360	50	102.8	80°C SCC
.15	D	3.0	1.2	1.4	-430	-370	7.0	30.3	Previously Used Solution SCC

Table : 10 Open Circuit Stress Corrosion Cracking Tests. 301 Y S.S.
 4.9 M NaCl, .15 M Na₂SO₄, 3 ml HCl/lit., 107^o C, deaerated.
 Loaded within 1 hour to 70% Y.S.

<u>% Def.</u>	<u>Def. Temp. (°C)</u>	<u>Stress (KSI)</u>	<u>E (mv S.C.E.) bef/ aft</u>	<u>pH bef/ aft</u>	<u>Time for E Shift (hrs)^{OC}</u>	<u>Time to Fail (hrs)</u>
0	—	32.0	-450/-380	.8/1.5	11.0	33.5
0	—	32.0	-450/-380	.7/1.5	11.1	34.5
15	+20	76.0	-450/-372	.7/1.3	7.3	16.5
15	+20	76.0	-465/-375	.7/1.3	7.9	17.8
25	+20	117.3	-450/-375	.5/1.3	6.0	9.0
25	+20	117.3	-455/-370	.8/1.5	—	9.7
50	+20	171.5	-450/-370	.6/1.3	6.3	9.5
50	+20	171.5	-450/-380	.6/1.2	7.9	9.3

TABLE:11 Open Circuit Stress Corrosion Cracking Tests. 301 Y S.S.
 4.9 M NaCl, .15 M Na₂SO₄, 3 ml HCl/lit., 107° C, deaerated.
 Loaded within 1 hour to 70% Y.S.

<u>% Def.</u>	<u>Def. Temp. (°C)</u>	<u>Stress (KSI)</u>	<u>E (mv S.C.E.) bef/ aft</u>	<u>pH bef/ aft</u>	<u>Time for E Shift (hrs)⁰⁰</u>	<u>Time to Fail (hrs)</u>
11	-196	114.5	-450/-375	.7/1.1	4.5	9.2
11	-196	114.5	-450/-375	.7/1.1	5.1	9.0
25	-196	193.6	-457/-380	.6/1.2	6.4	7.9
25	-196	193.6	-457/-382	.6/1.2	5.6	8.1
30	+150	85.7	-457/-390	.7/1.3	10.3	14.0
30	+150	85.7	-445/-390	.7/1.4	9.8	13.3

Table: 12 Open Circuit Stress Corrosion Cracking Tests. 301 γ S.S.
 4.9M NaCl, .15M Na₂SO₄, 3 ml HCl/lit., 107°C, deaerated.
 Loaded within 1 hour to 95% Y.S.

<u>Def.</u>	<u>Def. Temp. (°C)</u>	<u>Stress (KSI)</u>	<u>E (mv S.C.E.) bef/ aft</u>	<u>pH bef/ aft</u>	<u>Time for E_{oa} Shift (hrs)</u>	<u>Time to Fail (hrs)</u>
0	---	43.7	-450/-380	.7/1.4	11.3	25.9
0	---	43.7	-440/-380	.7/1.4	9.6	27.7
15	+20	103.2	-450/-375	.7/1.2	7.5	11.4
15	+20	103.2	-450/-368	.7/1.3	7.4	12.3
25	+20	159.2	-460/-380	.7/1.3	6.5	8.2
25	+20	159.2	-452/-382	.7/1.0	5.0	8.1
11	-196	155.3	-445/-355	.7/1.2	5.0	8.1
11	-196	155.3	-450/-375	.7/1.1	5.3	7.8
30	+150	116.3	-450/-435	.7/1.0	---	1.6*
30	+150	116.3	-450/-440	.7/1.0	---	1.5*

*Specimen did not SCC, corroded & necked.

Table 13: Open Circuit Stress Corrosion Cracking Tests. 301 Y S.S.
4.9 M NaCl, .15 M Na₂SO₄, 3 ml HCl/lit., 107° C, deaerated.
Loaded to 70% Y.S.

<u>% Def.</u>	<u>Def. Temp. (°C)</u>	<u>Stress (KSI)</u>	<u>E (mv S.C.E.) bef/ aft</u>	<u>pH bef/ aft</u>	<u>E_{OC} Shift/Load (hrs)</u>	<u>Time to Fail (hrs)</u>
0	---	32.0	-450/-380	.6/1.2	12.2/12.7	18.8
0	---	32.0	-460/-385	.7/1.5	12.0/22.0	20.2
15	+20	76.0	-437/-378	.5/.95	7.5/22.1	13.9
25	+20	117.3	-435/-370	.7/1.4	6.5/20.0	6.8
11	-196	96.1	-450/-375	.7/--	5.3/20.3	7.4

TABLE 14

APPLIED POTENTIAL (E_a) SCC TESTS. 4.9 M NaCl, .15M Na₂SO₄, 3 ml HCl/lt.
(107°C) DEAERATED, 70% Y.S.

% DEF.	DEF. TEMP. (°C)	E_a (mv)	E_{oc} (m)		pH		LOAD Time(hrs)	TTF (hrs)	COMMENTS
			bef.	aft.	bef.	aft.			
0		-400	-440	-	.8	1.2	1	NF 120	Current Cathodic
0		-380	-443	-	.6	1.2	1	NF 170	Current Cathodic
0		-360	-450	-	.5	1.7	1	23.0	SCC, Corrosion
0		-350	-450	-	.6	4.5	1	6.3	SCC, Corrosion
0		-370	-440	-370	.7	1.5	22	17.7	SCC
15	20	-410	-450	-	.6	1.2	1	NF 113	Pitting, No SCC
15	20	-390	-446	-	.7	1.5	1	NF 166	Pitting, No SCC
15	20	-380	-450	-	.7	1.1	1	67.0	Pitting, 1 Major SCC
15	20	-380	-460	-	.7	1.1	1	34.1	Pitting, SCC
15	20	-370	-450	-	.7	1.1	1	13.7	Pitting, SCC
15	20	-360	-450	-	.7	1.6	1	4.3	Pitting, Coarse, SCC
25	20	-410	-450	-	.6	1.1	1	NF 100	Cathodic Current
25	20	-390	-450	-	.6	-	1	NF 110	Cathodic Current
25	20	-380	-450	-	.6	.9	1	55.3	Cathodic Current
25	20	-380	-454	-	.7	-	1	6.4	Cathodic Current
25	20	-370	-450	-	.7	1.5	1	2.2	Anodic Current
50	20	-475	-453	-	.6	1.3	1	NF 100	No SCC
50	20	-450	-458	-	.6	1.4	1	45.2	SCC
50	20	-420	-450	-	.6	1.3	1	8.8	SCC
50	20	-400	-456	-	.6	-	1	NF 100	No SCC
50	20	-390	-456	-	.5	.9	1	97.0	SCC
50	20	-380	-450	-	.6	1.2	1	62.3	SCC
50	20	-370	-455	-	.5	1.0	1	5.0	SCC
11*	-196	-390	-400	-	.7	1.2	1	NF 165	No SCC
11*	-196	-380	-460	-	.7	-	1	19.4	1 Major SCC (Integranular)
11*	-196	-370	-460	-	.7	1.4	1	3.0	1 Major SCC
11	-196	-450	-452	-370	.6	1.2	20	NF 121	No SCC
11	-196	-420	-452	-373	.6	1.3	24	NF 131	No SCC, Crevice
11	-196	-400	-440	-370	.6	1.1	21	59.1	Pitting
11	-196	-380	-457	-373	.6	1.5	21	10.3	SCC

TABLE 14 (continued)

APPLIED POTENTIAL (E_a) SCC TESTS, 4.9 M NaCl, .15M Na₂SO₄, 3 ml HCl/lt.
(107°C) DEAERATED, 70% Y.S.

<u>% DEF.</u>	<u>DEF. TEMP. (°C)</u>	<u>E_a (mv)</u>	<u>E_{oc}(m)</u>		<u>pH</u>		<u>LOAD Time(hrs)</u>	<u>TTF (hrs)</u>	<u>COMMENTS</u>
			<u>bef.</u>	<u>aft.</u>	<u>bef.</u>	<u>aft.</u>			
25	-196	-475	-450	-382	.6	1.4	6	39.2	1 Major SCC (Intergran.)
25	-196	-450	-450	-378	.6	1.6	6	100	1 Major SCC (Intergran.)
25	-196	-420	-452	-369	.6	1.2	6	106	1 Major SCC (Intergran.)
25	-196	-400	-450	-375	.6	.9	6	NF 110	No SCC
25	-196	-390	-400	-370	.6	1.2	6	71.6	1 Major SCC
25	-196	-380	-460	-370	.6	1.2	8	3.0	1 Major SCC
30	+150	-400	-440	-370	.6	1.5	12	NF 112	No SCC
30	+150	-390	-440	-375	.7	1.3	11	NF 112	No SCC
30	+150	-380	-440	-370	.7	1.3	22	9.4	SCC
30	+150	-370	-445	-	.7	1.5	1	7.8	1 Major SCC

* 90% Y.S.

TABLE 15

E_{oc} , $E_{+ -}$, E_{cc} 301 AUSTENITIC STAINLESS STEEL
4.9 M NaCl, .15 M Na₂SO₄, 3 ml HCl/lt. 107°C. DEAERATED

<u>DEFORMATION</u>	<u>DEFORMATION TEMPERATURE (°C)</u>	<u>$E_{oc}(mv)$</u>		<u>$E_{cc}(mv)$</u>	<u>$E_{+ -}(mv)$</u>
		<u>bef.</u>	<u>aft.</u>		
0	-	-450	-380	- 375	- 375
15	+ 20	-450	-375	- 385	- 380
25	+ 20	-450	-375	- 385	- 375
50*	+ 20	-450	-375	- 395*	- 375
11	- 196	-450	-375	- 385	- 375
11 ⁺	- 196	-450	-375	- 410	- 375
25*	- 196	-455	-380	- 395*	- 385
30 ⁺	+ 150	-450	-390	- 385	- 375

* Failures at E_a more active than E_{cc}

+ Load After E_{oc} Shift

Fig. 1 Yield Strength vs. % deformation. 301 S. S.
Deformed by rolling.

STRESS CORR. CRACK.

FIG.2: SPECIMEN

- A - GAS INLET
- B - REFLUX CONDENSER
- C - THERMOMETER
- D - WORKING ELECTRODE
- E - COUNTER ELECTRODE
- F - POTENTIODYNE ANALYZER
- G - LUGGIN CAPILLARY
- H - REFERENCE ELECTRODE
- I - HEATER

Fig. 3. Polarization Cell.

Fig. 4. Stress Corrosion Cracking Apparratus.

Fig. 5. Polarization Curve: .1 M NaCl, .05 M Na₂SO₄, .5 ml HCl/lit., pH=2.35, 100°C, Deaerated.

Fig. 6. Polarization Curve. .1 M NaCl, .15 M Na_2SO_4 , pH=2.5, 100°C, Aerated.

Fig. 7. Polarization Curve. 301. .1 M NaCl, .15 M Na₂SO₄,
.5 ml HCl/lit. pH= 2.1, 100° C, Deaerated.

Fig. 8. Polarization Curve. .5 M NaCl, .1 M Na_2SO_4 , 1.0 ml HCl/lt., pH= 2.2, 100°C, Aerated.

Fig. 9 . Polarization Curve. .5 M NaCl, .15 M Na₂SO₄, 1.0 ml HCl/lt., pH=2.2, 100°C, Aerated.

Fig. 10. Polarization Curve. 301. .5 M NaCl, .05 M Na_2SO_4 ,
pH= 1.5, 100°C, Deaerated.

Fig. 11. Polarization Curve. 301. 1.0 M NaCl, .05 M Na_2SO_4 , pH= 1.5, 100° C, Deaerated.

Fig. 12. Polarization Curve. 301. 1.8 M NaCl, .05 M Na_2SO_4 , 3 ml HCl/lt., pH= 1.1, 103°C , Deaerated.

Fig. 13. Polarization Curve. 301. 2.9 M NaCl, .05 M Na_2SO_4 , 3 ml HCl/lt., $\text{pH} \approx 1.2$, 103°C , Deaerated.

Fig. 14. Polarization Curve. 3.9 M NaCl, 3.0 ml HCl/lit., pH = .6, 105°C, Deaerated.

Fig. 15. Polarization Curve. 301. 3.9 M NaCl, .05 M Na_2SO_4 , 1.0 ml HCl/lt., pH= 1.3, 105°C . Deaerated.

Fig. 16. Polarization Curve. 301, 3.9 M NaCl, .15 M Na_2SC_4 , 1.5 ml HCl/lit., pH 1.2, 105°C , Deaerated.

Fig. 17. Polarization Curve: 3.9 M NaCl, .15 M Na_2SO_4 , 3.0 ml HCl/lit., pH .85, 105°C, Deaerated.

Fig. 18. Polarization Curve. 301. 4.9 M NaCl, .15 M Na_2SO_4 ,
pH= 6.1, 107°C , Deaerated.

Fig. 19. Polarization Curve, 301. 4.9 M NaCl, .15 M Na_2SC_4 , 1.0 ml HCl/lt., pH= 1.3, 107°C , Deaerated.

Fig. 20. Polarization Curve. 4.9 M NaCl, 2.0 ml HCl/lit, pH= .7,
107° C, Deaerated.

Fig. 21. Polarization Curve. Annealed 301.
1.5M NaCl, .05 M Na₂SO₄, 2.5 ml HCl/lit.
pH=1.5, 103° C, deaerated.
Sweep rate 500 mv/hr.

Fig. 22. Polarization Curve. Annealed 301.
 1.8 M NaCl, .05 M Na₂SO₄, 5 ml HCl/lit.,
 pH= 1.0, 103°C, deaerated.
 Sweep rate 500mv/hr.

Fig. 23. Polarization Curve. Annealed 301.
 4.9 M NaCl, .15 M Na₂SO₄, 3 ml HCl/lit.,
 pH= .7, 107° C, deaerated.
 Sweep rate 500 mv/hr.

Fig. 24. Open Circuit Stress Corrosion Cracking Test. Annealed 301.
1.8 M NaCl, .05 M Na₂SO₄, 5 ml HCl/lit. pH = 1.0/4.4. 103° C, deaerated.
Loaded to 32 KSI (70% Y.S.).

Fig. 25.

SCC Test, $E_a = -250$ mv. Annealed 301, 1.8 M NaCl, .05 M Na_2SO_4 , 5.0 ml HCl/lt.,
 pH= 1.4/2.0, Deaerated, 103°C , Anodic Current.

Fig. 26. SCC Test, $E_a = -200\text{mv}$, Annealed 301, 1.8 M NaCl, .05 M Na_2SO_4 , 5.0ml HCl/lt., pH= 1.0/4.4, Deaerated, 103°C , Anodic Current.

Fig. 27. SCC Test, Open Circuit. Annealed 301. 4.9 M NaCl, 3.0 ml HCl/lit., pH = .3/1.4, 107°C, Deaerated.

Fig. 28. SCC Test, Open Circuit. Annealed 301. 4.9 M NaCl, .15 M Na_2SO_4 , 3 ml HCl/lit.
pH= .7/1.3, 80° C, Deaerated.

Fig. 29. SCC Test, Open Circuit. Annealed 301. Used 4.9 M NaCl, .15 M Na₂SO₄, 3 ml HCl/lit.
pH= 1.2/1.4, 107° C, Deaerated.

Fig. 30. SCC Test, Open Circuit, Annealed 301. 4.9 M NaCl, .15 M Na_2SO_4 , 3 ml HCl/lit.
pH = .6/1.5, 107°C , Aerated.

Fig. 31. Open Circuit Stress Corrosion Cracking Test, Annealed 301.
4.9 M NaCl, .15 M Na₂SO₄, 3 ml HCl/lit., 107° C, deaerated. Loaded to 70% Y.S.

Fig. 32. Open Circuit Stress Corrosion Cracking Test. Annealed 304.
4.9 M NaCl, .15 M Na₂SO₄, 3 ml HCl/lit. pH=.6/1.2. 107° C, deaerated.
Loaded to 70% Y.S.

Fig. 33. Polarization Curve. Annealed 301.
4.9 M NaCl, .15 M Na₂SO₄, 3 ml HCl/lt. pH=.7.
107° C, deaerated. Immersed 1 hour.
Sweep rate 500 mv/hr.

Fig. 34. Time to fail vs. % deformation. 301 S. S.
4.9 M NaCl, .15 M Na₂SO₄, 3ml HCl/lit.
107° C, deaerated. Loaded to 70% Y. S.
Deformed at +20° C.

Fig.35. Open Circuit Stress Corrosion Cracking Test. Annealed 301.
4.9 M NaCl, .15 M Na₂SO₄, 3 ml HCl/lit. pH= .8/1.5. 107° C, deaerated.
Loaded to 70% Y.S.

Fig. 36. Open Circuit Stress Corrosion Cracking Test. Deformed 15% at +20° C.
 4.9 M NaCl, .15 M Na₂SO₄, 3 ml HCl/lit., pH = .65/1.25. 107° C, deaerated.
 Loaded to 70% Y. S.

Fig. 37. Open Circuit Stress Corrosion Cracking Test. Deformed 25% at +20° C.
4.9 M NaCl, .15 M Na₂SO₄, 3 ml HCl/lit., pH=.5/1.3, 107° C, deaerated.
Loaded to 70% Y.S.

Fig. 38. Open Circuit Stress Corrosion Cracking Test. Deformed 50% at +20° C.
 4.9 M NaCl, .15 M Na₂SO₄, 3 ml HCl/lit., pH = .6/1.3. 107° C, deaerated.
 Loaded to 70% Y. S.

Fig. 39. Time to fail vs. % deformation. 301 S. S.
 4.9 M NaCl, .15 M Na_2SO_4 , 3ml HCl/lit.
 107° C, deaerated. Loaded to 70% Y. S.

Fig. 40. Open Circuit Stress Corrosion Cracking Test. Deformed 30% at $+150^{\circ}\text{C}$.
 4.9 M NaCl, .15 M Na_2SO_4 , 3 ml HCl/lit., pH=.7/1.25. 107°C , deaerated.
 Loaded to 70% y.s.

Fig. 41. Time to fail vs. % deformation. 301 S. S.
 4.9 M NaCl, .15 M Na₂SO₄, 3ml HCl/lit.
 107° C, deaerated. Loaded to 95 % Y. S.

Fig. 42. Open Circuit Stress Corrosion Cracking Test. Annealed.
 4.9 M NaCl, .15 M Na_2SO_4 , 3 ml HCl/lit., pH = .6/1.2. 107°C , Deaerated.
 Loaded to 70% Y.S.

Fig. 43. Open Circuit Stress Corrosion Cracking Test. Annealed 301. 4.9 M NaCl, .15 M Na_2SO_4 , 3 ml HCl/lit. pH= .7/1.5. 107° C, deaerated. Loaded to 70% Y. S. after 22 hrs.

Fig. 44. SCC Test, Open Circuit. Deformed 15% at 20°C. 4.9 M NaCl, .15 M Na₂SO₄, 3 ml HCl/lit., pH= .5/1.6, 107°C, Deaerated, Loaded to 70% Y.S.

Fig. 45. Open Circuit Stress Corrosion Cracking Test. Deformed 25% at +20° C.
 4.9 M NaCl, .15 M Na₂SO₄, 3 ml HCl/lit., pH = .65/1.4. 107° C, deaerated.
 Loaded to 70% Y.S.

Fig. 46. Open Circuit Stress Corrosion Cracking Test. Deformed 11% at -196°C .
 4.9 M NaCl, .15 M Na_2SO_4 , 3 ml HCl/lit., pH = .7/---. 107°C , deaerated.
 Loaded to 60% Y.S.

Fig. 47. Current vs. Time, Annealed, Applied Potential = -360 mV, 4.9 M NaCl, .15 Na₂SO₄, 3.0 ml HCl/lit, initial pH = .51, final pH = .65, 107°C. Deaerated. Anodic Current.

Fig. 48. Current vs. Time; Annealed, Applied Potential = -380 mV, 4.9 M NaCl, $.15$ M Na_2SO_4 , 3.0 ml HCl/Hf, initial pH = $.60$, final pH = 1.20 , 10°C .

Fig. 49. SCC Test, $E_a = -370$. 301, Deformed 15% at 20°C . 4.9 M NaCl, .15 M Na_2SO_4 , 3 ml HCl/lit., pH = .7/1.1, 107°C , Deaerated. Anodic Current.

Fig. 50. SCC Test, $E_a = -410$. 301. Deformed 15% at 20°C . 4.9 M NaCl, .15 M Na_2SO_4 , 3 ml HCl/lt., pH = .6/1.2, 107°C , Deaerated.

Fig. 51. Time to Fail vs. Potential. Annealed 301.
 4.9 M NaCl, .15 M Na₂SO₄, 3 ml HCl/lit. pH=.7.
 107° C, deaerated. Loaded to 70% Y.S.
 E_{cc}=-375.

Fig. 52 . Time to Fail vs. Potential. 301 deformed 15% at 20°C.
 4.9 M NaCl, .15 M Na₂SO₄, 3 ml HCl/lit., loaded to 70%
 Y.S. E_{cc} = -385.

Fig. 53. Time to Fail vs. Potential. 301 deformed 25% at +20° C. 4.9M NaCl, .15M Na₂SO₄, 3 ml HCl/lit. pH=.7, 107° C, deaerated. Loaded to 70% Y.S. E_{cc}=-385.

Fig. 54 . Time To Fail vs. Potential. Deformed 30% at +150° C.
 4.9 M NaCl, .15 M Na₂SO₄, 3 ml HCl/lt., pH=.7, 107° C,
 deaerated. Loaded to 70% Y.S.
 E_∞ = -385.

Fig. 55. Time to Fail vs. Potential. 301 deformed 50% at 20°C.
 4.9 M NaCl, .15 M Na₂SO₄, 3 ml HCl/lit., 107°C, deaerated
 E_{cc} = -3. 1 hour immersion.

Fig. 56 . Time to Fail vs. Potential. 301 deformed 25% at -196°C .
 4.9 M NaCl, .15 M Na_2SO_4 , 3 ml HCl/lit., 107°C , deaerated.
 $E_{cc} = -385\text{mv}$. Allowed Potential to shift before applying
 load, 6 hours immersion before loading.

Fig. 57. Time to Fail vs. Potential. 301 deformed 11% at -196°C . 4.9 M NaCl, .15 M Na_2SO_4 , 3 ml HCl/lit. pH=.7, 107°C , deaerated. Loaded to 70% Y.S. $E_{cc}=-385$. Loaded after one hour immersion.

Fig. 58 . Time to Fail vs. Potential. 301 deformed 11% at -196°C .
 4.9 M NaCl, .15 M Na_2SO_4 , 3 ml HCl/lit., pH=.7, 107°C ,
 deaerated. Loaded to 70% Y.S. $E_{cc} = -410$ mv. Loaded
 after E_{oc} shift.

Fig. 59. Micrograph. Unetched.
Annealed. Open Circuit. 320X.

Fig. 60. Micrograph. Etched.
Annealed. Open Circuit. 480X.

Fig. 61. SEM Micrograph.
Deformed 25 % at -196°C .
Ea= -450. 1000X.

Fig. 62. Energy Dispersive X-Ray Analysis.
301, Annealed. Unexposed. 1200X.

Fig. 63. Energy Dispersive X-Ray Analysis. 301, annealed, exposed 2 hours. 1200X.

Fig. 64. Energy Dispersive X-Ray Analysis. 301, annealed, exposed 48 hours. 1200X.