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Report COO-2018-24 (Q-8, 9, & 10 and
Final Report)

STRESS CORROSION CRACKING OF Fe-Cr-Ni ALLOYS
IN CAUSTIC ENVIRONMENTS

A. K. Agrawal and R. W. Staehle
Department of Metallurgical Engineering

October 15, 1970 - June 30, 1971

U. S. Atomic Energy Commission
Chicago Operations Office
Argonne, Illinois

Contract No. AT(11-1)-2018

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RF Project 2765

Report No. COO-2018-24

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To U. S. ATOMIC ENERGY COMMISSION
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois 60439
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On STRESS CORROSION CRACKING OF Fe-Cr-Ni ALLOYS
IN CAUSTIC ENVIRONMENTS

For the period October 15, 1970 - June 30, 1971

Submitted by A. K. Agrawal and R. W. Staehle
Department of Metallurgical Engineering

Date June 30, 1971

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1.0 ABSTRACT

Results from stress corrosion and electrochemical studies are reported for Fe-Cr-Ni alloys exposed to NaOH-H₂O solutions and fused NaOH. Due to the lack of funds to support the research, this is the last report. A certain minimum stress, temperature, and caustic concentration is required for propagation of stress corrosion cracking in stainless steel 304. The rate of SCC is maximum at 70% yield stress. Stainless steel 304 in boiling 60% NaOH undergoes partial anodic protection between the potentials -750 and -100 mV_H. Failure times in this range is considerably lower than at other potentials. The Fe-20Cr-Ni ternaries in 19.5N NaOH above -550 mV (SCE) corrode at a faster rate, due to high transpassive corrosion rate of Cr, than pure Fe or Fe-Ni binaries.

2.0 CONCLUSIONS

1. The stress corrosion cracking of annealed 304 stainless steel does not occur at temperatures below 120°C in caustic solutions $\leq$ 80% NaOH. The minimum caustic concentration required for SCC at a load equivalent to 50% yield stress is $>$ 60% NaOH. The failure time in boiling NaOH decreases with an increase in applied stress but, a minima occurs at 70% yield stress. The failure time at minima is approximately one-half of that for either 60 or 80% yield stress.

The corrosion potential of 304 stainless steel becomes more negative with increase in temperature and falls suddenly to low values at a particular temperature. This temperature decreases with increase in caustic concentration. Failures in boiling 60% NaOH are rapid at active dissolution potentials (-850 to -750 mV_H) and at potentials (-100 to +250 mV_H) where higher oxides (e.g., Fe₂O₃) are formed. Rapid failure is the result of high currents at those potentials. At other potentials currents are low and failure is slow.

2. Preliminary results of tests with stressed foils of Incoloy-800, and stainless steels 304, 316, and 430 exposed to high temperature and high humidity caustic-chloride environment show intergranular and pitting corrosion.

3. Photographs of special nickel cells constructed for electrokinetic corrosion and stress corrosion studies in fused NaOH environment are presented.

4. The corrosion rate of Fe-Ni binaries in 19.5N NaOH is less than that of pure Fe but greater than that of pure Ni. The corrosion rate of Fe-20Cr-Ni ternaries below -550 mV (SCE) is intermediate between pure Fe and pure Ni but, at nobler potentials corrosion rate is higher than that of pure Fe. The higher rate is due to Cr corroding at a faster rate (than Fe) in its transpassive region.

3.0 INTRODUCTION

This work is being conducted in support of the LMFER activities to identify the possible incidences and extent of caustic stress corrosion cracking which could cause premature equipment failure. The most likely sites where such SCC is possible are (1) in the steam generator at the Na-H₂O interface and (2) on exterior surfaces where Na spills or leaks can hydrolyze to form NaOH solutions in the presence of moisture.

Caustic SCC is a serious consideration in iron base alloy systems and becomes generally more serious with increasing iron concentrations in the alloy as shown in Report COO-2018-4.

This program is approaching the problem by conducting both direct SCC studies and fundamental studies aimed at understanding the phenomenon. The work is outlined in a series of tasks. Work performed on a given task is described. Note that work is not performed each quarter on all tasks owing to schedule for starting the respective task and also to vagaries in academic schedules for graduate students.

4.0 PROGRESS IN INDIVIDUAL TASKS

Task 1 - Tests of Engineering Geometries

A. Aims

The purpose of this work is to conduct experiments which simulate possible failure modes in engineering geometries for the purpose of finding what kind of corrosion phenomena might occur in the event of a sodium leak. From this information more specific definitions could be given to fundamental studies.

B. Results

Work suspended.

Task 2 - General Effects of Alloy and Environmental Composition in Aqueous Solvents on Stress Corrosion Cracking (D. V. Subrahmanyam)

A. Aims

The purpose of this task is to assess the general effects of environment and alloy chemistry on the incidence of caustic stress

corrosion cracking. Variables will include alloy chemistry, temperature, concentration of OH^- , identity of cation, dissolved gases including oxygen, and electrochemical potential.

B. Results

1. Introduction

The effects of NaOH concentration, heat treatment, and that of applied potential in boiling 50% NaOH on the SCC behavior of 304 stainless steel have been described in the previous reports, Q-5 to Q-7. The present work describes SCC behavior of 304 stainless steel in various caustic solutions as a function of temperature and stress level and, as a function of applied potential in boiling 60% NaOH.

2. Experimental

The specimens were 15 mil diameter wires annealed at 2200°F for two hours and air cooled. Specimen loading and the other experimental details are given in the previous reports.

2.1 Open-circuit cracking - The wires were subjected to constant load in 60, 70, and 80% NaOH solutions under the following conditions,

- (i) Stress - 50 to 150% of yield stress (i.e., 8,690-26,070 psi)
- (ii) Temperature - 80 to 160°C

The corrosion potential was measured during these experiments.

2.2 Potentiostatic cracking - The effect of applied potential on the failure time and crack morphology were studied in boiling 60% NaOH solution. A constant load equal to 100% of yield stress (17,380 psi) was used. Potentiostatic polarization curves of stressed and unstressed specimens were also obtained.

3. Results

3.1 Effect of temperature and stress on failure time - Figure 1 shows the effects of temperature on failure time in 70 and 80% NaOH solutions. There were no failures at temperatures below 120°C; it occurred at 120°C and above. Failure in 60% NaOH solution occurred only at the boiling point 135°C. The load was 100% of yield stress in all the above cases.

Figure 2 shows the effect of stress level on failure times. No failure occurred at 50% y.s. load in boiling 60% NaOH. However, at this load failures occurred in 100-130 hours in 70 and 80%

Fig. 1 - Effect of temperature on failure time

Fig. 2 - Effect of applied stress on failure time

boiling NaOH. In general, failure time decreased with increase in stress. A minima is observed at a load equivalent to 70% y.s. (in 70 and 80% NaOH). The failure time at this stress is approximately one-half of that for either 60 or 80% y.s.

3.2 Effect of temperature and stress on corrosion potential-
The effect of temperature on corrosion potential of stressed 304 stainless steel is shown in Fig. 3. Corrosion potential as a function of temperature was also measured in 50% NaOH solution and is included in the above figure. The difference between the corrosion potentials of stressed and unstressed specimen was insignificant.

The corrosion potentials became more negative (cathodic) with the increase in temperature and caustic concentration. This shift was continuous but for an abrupt drop at a particular temperature, e.g., the drop is ~ 550 mV in 70% NaOH between 90 and 100°C. The temperature at which this drop occurs decreases with an increase in caustic concentration.

Figure 3 shows a set of two corrosion potential curves for each caustic concentration (except for 50% NaOH). The curves 2, 4, and 6 show the values that were obtained after 17 hours. The curves 3, 5, and 7 show the values measured at the end of the run. The later corrosion potential values are slightly more negative than the first ones.

3.3 Effect of applied potential on failure time, current-time curve, and crack morphology in boiling 60% NaOH solution - The polarization curves of unstressed and stressed material are shown in Fig. 4. The curves 1 and 2 show the steady state values of current and curve 3 shows maximum current recorded during polarization. The polarization curve 1 for the unstressed specimen exhibits an active dissolution range between -950 to -800 mV_H. The active peak current is $500 \mu\text{A}$ at -850 mV_H. The passive range lies between -800 to -400 mV_H and, the lowest current observed is $15 \mu\text{A}$. The transpassive dissolution starts at -400 mV_H and extends up to -150 mV_H. Current at the transpassive peak, $7000 \mu\text{A}$ at -150 mV_H, is considerably higher than at the active dissolution peak. A Tafel behavior with a 70 mV slope is observed in the transpassive range. Higher metal oxides are formed at potentials more noble than -150 mV_H. Stressing did not significantly alter the polarization behavior, curve 2. One noticeable change was the narrowing of the transpassive dissolution range and consequent absence of the Tafel. This region is completely absent in the potential vs. maximum current plot, curve 3.

The potential vs. failure time plot is shown alongside polarization curves in Fig. 4. Rapid failures occurred in the active dissolution range (-850 to -750 mV_H) and in the region where higher valence oxides are formed (-100 to $+250$ mV_H). Between these two regions the failure times were prolonged.

Fig. 3 - Effect of temperature on corrosion potentials .

Fig. 4 - Potentiostatic polarization curves and effect of applied potential on failure time

The current vs. time plots (on log-log scale) at various potentials for stressed specimens are shown in Figs. 5A and 5B. The main features of these plots are described below.

- (i) Potential +245 mV_H (Curve 1): Current decreased linearly with time exhibiting anodization.
- (ii) Potential +45 mV_H (Curve 3): Current decreased linearly for 20 minutes then gradually increased to a plateau and decreased again.
- (iii) Potentials +145, -255, and -455 mV_H (Curves 2, 4, and 5): Current increased linearly up to 300-1000 minutes and, after some lowering, rose sharply and then dropped to low values.
- (iv) Potentials -555 and -655 mV_H (Curves 6 and 7): Current behaved as in (iii) but the lowering after the linear increase was more steeped.
- (v) Potentials -755 and -855 mV_H (Curves 8 and 9): Current increased with time up to 1000 minutes and then dropped.
- (vi) Potential -955 mV_H (Curve 10): This potential was 30 mV more negative than the open circuit corrosion potential and, as a result, the current obtained was cathodic. Cathodic current increased up to 140 minutes and then cusped.

Figure 6 shows the photomicrographs of the specimens failed at different potentials. The mode of cracking changed with lowering of the potential from +245 to -955 mV_H. It is described below:

- (i) Potentials +245 and +145 mV_H: The failure was by pitting.
- (ii) Potentials -255 to -655 mV_H: The attack was mixed type, intergranular and transgranular, and exhibited blunted cracks.
- (iii) Potential -855 mV_H: The failure was by general corrosion which was rather severe. Reduction in the specimen's area is evident.
- (iv) Potentials -940 and -955 mV_H: The failure at corrosion potential, -940 mV_H, was by both intergranular and transgranular cracking. The

Fig. 5A - Current-time plots in boiling 60% NaOH in the potential range +245 to -455 mV_H.

Fig. 5B - Current-time plots in boiling 60% NaOH solution in the potential range -555 to -955 mV_H

+245 mV_H

500X

+145 mV_H

500X

-255 mV_H (not failed)

150X

-355 mV_H

150X

Fig. 6 - Effect of applied potential on crack morphology (60% NaOH; load: 100% of y.s.)

-555 mV_H

150X

-655 mV_H

500X

500X

Fig. 6 - (continued)

-955 mV_H (unstressed)

150X

-955 mV_H

150X

-940 mV_H(E_{corr})

150X

Fig. 6 - (continued)

photomicrograph of unstressed specimen at -955 mV_H, shown for comparison purposes, exhibits little corrosion.

4. Discussion

4.1 Effect of temperature on failure time - The minimum temperature required to produce cracking was dependent upon the concentration of the hydroxide solution. Changes in corrosion potential with temperature was also concentration dependent. The above two phenomena can be qualitatively correlated and, in turn, explained using the potential-pH diagrams at required temperatures.

Pourbaix diagrams at elevated temperatures (30-300°C) for Fe and Ni have recently been published¹⁻³ but, for Cr it is still not available. A significant change observed at elevated temperatures is the expanded stability zone of HFeO_2^- and HNiO_2^- anions. At 100°C and pH 15-15.3 the anion HFeO_2^- is stable between -1400 and -760 mV_H. As the temperature is further increased to 150°C, the stability zone in the same pH range increases to -1625 to -820 mV_H. Similarly, for HNiO_2^- in the pH 15-15.3 the stability zones at 100°C and 200°C are -1200 to +250 and -1600 to +150 mV_H, respectively. At 25°C and pH ~ 15.5 the stability range for CrO_3^{3-} anion is -1400 to -200 mV_H.⁴ It is reasonable to assume that CrO_3^{3-} anion exists over a wider potential range at elevated temperatures 100-150°C. At potentials more noble than the respective upper limits of stability of these anions oxides are formed -- Fe_3O_4 , Fe_2O_3 for Fe; Ni_3O_4 , Ni_2O_3 for Ni; and Cr_2O_3 for Cr.

The values of corrosion potential as a function of pH at various temperatures is listed in Table I. The effect of pH on corrosion potential at these temperatures is also shown in Fig. 7. The plots show increase in pH dependence with increase in temperature.

Table I - Effect of pH on Corrosion Potential at Different Temperatures

Conc. of NaOH (Wt.%)	Conc. of NaOH (M)	pH at 25°C	E_{corr} (mV _H)			
			Temp. (°C)			
			90	100	120	130
50	12.5	15.10	-215	-215	-240	-300
70	17.5	15.24	-290	-310	-650	-910
80	19.8	15.30	-320	-890	-920	-935

The values of corrosion potential in 50% NaOH (pH 15.1) up to 125°C lie in a potential region where the formation of Fe_2O_3 type oxide is predicted by the Pourbaix diagrams. Under these conditions, Ni and Cr are still in the form of their anions. Probably, due to slow

Fig. 7 - Effect of pH on corrosion potential at different temperatures.

rate of production of these anions, the cracking does not occur in the above environment. A similar condition exists up to pH 15.24 (70% NaOH) and 120°C. However, at 130°C corrosion potential falls into a region where HFeO_2^- is formed, and hence stress corrosion cracking occurs. At pH 15.3 (80% NaOH) and temperatures above 90°C the observed corrosion potentials correspond to the HFeO_2^- formation region; but cracking did not take place until a temperature of 125°C was reached. This could be due to (i) slow production rate of the HFeO_2^- anion, and (ii) low velocity of dislocation at these temperatures. The second aspect needs a careful study by electron microscopy.

Considering failure time to be a measure of reaction rate dependent upon temperature and, following Arrhenius equation, the energy of activation was calculated 15 kcal from failure time vs. $1/T$ plot, Fig. 8.

4.2 Effect of stress on failure time - The stress vs. failure time relation shows anomalous behavior, i.e., the considerable lowering of failure time at 70% y.s. Smialowski and Rychick⁵ have also reported similar effects of stress in boiling MgCl_2 solutions. According to them, applied stress changes the dislocation arrangements from planar type at low stresses to cellular type at higher stresses. Planar dislocations is easily breakable by plastic deformation, and thus the material is more susceptible to cracking.⁶⁻⁷ Greely et al.⁸ accounted their findings on the similar effect in chloride medium as due to the formation of a quasi-martensite phase. Further studies with metallography and electron microscopy are needed to elucidate the above viewpoints.

4.3 Effect of applied potential - The mode of cracking is potential dependent. Stress corrosion cracking took place at a potential close to open-circuit (corrosion) potential. At more noble potentials the mode changed, general corrosion in the active dissolution range, cracking with little or no crack repassivation in the passive range, and pitting in the transpassive range. These changes correspond to the formation (as dictated by the potential pH diagrams) of different species $\text{HFeO}_2^- \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_2\text{O}_3$, etc. on specimen surface.

In Fig. 9 failure time is shown marked on the maximum current vs. potential plot. The failure time increased with a fall in current and it was maximum at lower currents.

The humps and depressions after the linear branch (in the current-time plots, Figs. 5A and 5B,) correspond to the dissolution and passivation events. The initial branch, 1000 minutes, of the curve at +245 mV_H is replotted on a linear scale in Fig. 10. Using the area under this curve and assuming 100% anodization (Fe_2O_3) efficiency, the film thickness on the specimen surface was calculated to be $2.5-3 \times 1000 \text{ \AA}$. A heavy black oxide coating on the specimen was seen during the experiments.

Fig. 8 - Effect of temperature on failure time - Arrhenius plot

Fig. 9 - Failure time on maximum current vs. potential plot

Fig. 10 - Current-time curve in 60% NaOH at +245 mV_H

The present potentiostatic experiments indicate no possibility of applying either anodic or cathodic protection to 304 stainless steel in the high-temperature high-caustic environment.

Task 3 - General Effect of Alloy and Environmental
Composition on Stress Corrosion Cracking
in Sodium Base Environments Containing NaOH

A. Aims

The purpose of this task is to perform a parallel program to that in Task 2 except for the environment being a sodium base.

B. Results

Work suspended.

Task 4 - Dissolution and Passivation Behavior

(Kaye Poteet and G. Theus)

A. Aims

This task is aimed at obtaining information on the kinetics of oxidation and reduction processes in electrochemically accessible (i.e., ionically conducting) environments. This includes aqueous and fused salt environments as opposed to liquid metals. This work will define those regions where activated dissolution and passivation occur as a function of alloy, temperature, and environmental composition. The definition of these regions will provide a guide to where stress corrosion might occur and also will provide direct information on corrosion rates.

B. Results

1. Introduction

Results of the electrokinetic studies of Fe-Cr-Ni alloys in aqueous caustic solutions, 1 to 10N NaOH, have been reported in the previous four reports. Results of the experiments in ~20N NaOH; and a few in 10N NaOH, are presented here.

A special cell and associated apparatus recently acquired for the work in fused NaOH is also described.

2. Experimental

The apparatus and experimental procedure used for polarization studies in 80% NaOH (19.5N NaOH) solution were similar to that used with dilute solutions and are given in COO-2018-18 (Q-5).

Additional experiments were performed to observe current vs. time behavior of specimens near their passive peaks. After a specimen attained its steady state corrosion potential, it was potentiostated at a passive potential. Current was recorded until it became steady-constant for an hour.

3. Results

(a) 19.5N NaOH--The anodic and cathodic polarization of pure metals Fe, Cr, and Ni, and their seven alloys were studied in 19.5N NaOH at 25° and 150°C. The decay of current with time near the passive peak potential was recorded for only pure Ni and seven alloys. The composition of alloys used in this work is given in COO-2018-8 (Q-3).

(i) Corrosion potential. The steady state corrosion potential of metals in 19.5N NaOH at 25 and 150°C are listed in Table II. The corrosion potential became more cathodic with increase in temperature. Chromium was an exception; its corrosion potential became more noble with an increase in temperature, -720 mV (SCE) at 25° and -500 mV (SCE) at 150°C. The cathodic shift was maximum for Fe (-100 mV) and least for Ni. The effect of Ni addition to Fe, Fe-Ni, and Fe-20Cr-Ni was to shift their corrosion potentials to more noble values. The corrosion potential of 80Ni-20Cr was close to that of Ni.

Table II - Corrosion Potential of Fe-Cr-Ni Alloys
in 10N and 19.5N NaOH

Alloy No.	Composition	Corrosion Potential, V(SCE)		
		10N NaOH	19.5N NaOH	
		118°C	25°C	150°C
1	100Fe		-1.15	-1.25
2	95Fe-5Ni	-1.15	-1.15	-1.20
3	90Fe-10Ni	-1.14	-1.14	-1.18
4	80Fe-20Ni	-1.05	-1.11	-1.11
12	100Ni	-0.97	-0.99	-1.00
51	80Fe-20Cr	-1.22	-1.16	-1.26
55	60Fe-20Cr-20Ni	-1.01	-1.04	-1.14
58	35Fe-20Cr-45Ni	-0.99	-1.10	-1.07
62	20Cr-80Ni	-0.96	-0.98	-1.11
	100Cr		-0.72	-0.50

(ii) Anodic polarization. Figures 11 through 13 show anodic polarization curves in 19.5N NaOH at 25°C. The current density (and, hence, corrosion rate) of Fe is greater than that of Ni by one and one-half order of magnitude between their respective corrosion and transpassive potentials, Fig. 11. The anodic polarization of Cr yielded only a passive-transpassive curve, indicating that its corrosion potential is in the passive region. Therefore, its corrosion rate cannot be fully ascertained and compared with that of the other two metals. Metals Fe and Ni show a second anodic peak. The peak is in the upper half of the passive region and, in the case of Ni, it is close to its transpassive potential. The current density at the second peak, in both cases, is higher than that at their respective first anodic (active) peak.

Polarization curves of Fe-Ni binaries in Fig. 12 show that the current densities are intermediate between that of Fe and Ni. Unlike pure Fe and Ni, binary curves show a near perfect passive region. The second anodic peak of either Fe or Ni is absent from 95Fe-5Ni and 90Fe-10Ni. In the case of 80Fe-20Ni, only a reduced second anodic peak of Ni is present.

Anodic polarization curves of 80Fe-20Cr, 80Ni-20Cr, and ternaries at 25°C are given in Fig. 13. The current density of 80Fe-20Cr between its corrosion potential, -1160 mV(SCE) and -400 mV(SCE), is lower by one order of magnitude than the corresponding current density for Fe. The current density at the second anodic peak of 80Fe-20Cr, which is sharp and near the second anodic peak of Fe, is slightly higher than the corresponding Fe peak. The polarization curve of 80Ni-20Cr between its corrosion potential, -980 mV(SCE) and -600mV(SCE), has characteristics similar to that of Ni. At higher potentials, current density is higher because of large transpassive Cr current. The combined effect of large transpassive Cr current and the second Ni peak is multiple (three) anodic peaks between potentials 0 and 200 mV(SCE). Polarization curves of Fe-20Cr-Ni ternaries are similar to that of 80Fe-20Cr but the current density is slightly lower. The lowering increases with the Ni addition.

Results of anodic polarization in 19.5N NaOH at 150°C are shown in Figs. 14 through 16. The primary effect of higher temperature is increased kinetics--a two decade increase in current density in all cases, i.e., pure metals and alloys. The corrosion potential of Cr shifted completely to transpassive region and thus yielding only transpassive curve, Fig. 14. The second anodic peak of Fe moved from the upper half of the passive range to the lower half, -200 to -850 mV(SCE). The first anodic peak of Ni is sharpened and, thus, causing complete passivation within 10 mV of peak potential. Polarization curves of Fe-Ni binaries at 150°C show an additional anodic peak near (~50 mV) the first peak. Otherwise, the shape of curves is identical to that at 25°C. Polarization curves of (80Fe-20Cr, 80Ni-20Cr, and Fe-20Cr-Ni) Cr-containing alloys have become very complex; the number of anodic peaks have multiplied to four. The complete passivation region is practically absent from these alloys and thus, making them unsuitable for anodic protection.

Fig. 11 - Anodic polarization behavior of Fe, Cr, and Ni in 19.5N NaOH at 25°C

Fig. 12 - Anodic polarization behavior of Fe-Ni binaries in 19.5N NaOH at 25°C

Fig. 13 - Anodic polarization behavior of Fe-20Cr-Ni alloys in 19.5N NaOH at 25°C

Fig. 14 - Anodic polarization behavior of Fe, Cr, and Ni in 19.5N NaOH at 150°C

Fig. 15 - Anodic polarization behavior of Fe-Ni binaries in 19.5N NaOH at 150°C

Fig. 16 - Anodic polarization behavior of Fe-20Cr-Ni alloys in 19.5N NaOH at 150°C

An attempt was made to interpret anodic polarization curves of pure metals according to their respective Pourbaix diagrams. The analysis is shown in Fig. 17, possible chemical species existing at various potentials are marked against their corresponding polarization curve. Figure 17 indicates only the thermodynamic possibility rather than the actual situation. In the passive region there may be more than one oxide present at any potential. The nature (and composition) of passive film is still an unsettled subject.

(iii) Cathodic polarization. Cathodic polarization curves in 19.5N NaOH at 25 and 150°C are shown in Figs. 18 through 23. The Tafel slope of H₂ evolution reaction at 25°C is ~70 mV. The slope at 150°C is ~100 mV for Cr and Ni, but ~50mV for Fe and all the alloys. The Tafel at 25°C does not become distinct until a 10-15 $\mu\text{A}/\text{cm}^2$ current density is reached, and at 150°C the current density required is ~1000 $\mu\text{A}/\text{cm}^2$.

During the cathodic polarization of Cr it passes from its passive corrosion potential through its passive region and directly to H₂ evolution region. The active dissolution portion is absent; probably because of the current density of H₂ evolution being much higher than that of the active dissolution reaction. (In the other cases, corrosion potentials are in their active dissolution region.)

(iv) Current vs. time plots. Current vs. time plots at fixed passive potentials in 19.5N NaOH at 25 and 150°C are shown in Figs. 24 through 27. In almost all cases, the trend is identical. At the moment a potential is applied, the value of current is high, which then gradually falls and, finally, becomes steady. The value of steady state current at any temperature is both potential and (alloy) composition dependent. The effect of alloying and temperature is summarized in Fig. 28. The effect of temperature is increased kinetics, by a factor of two decades. The rate of passivation of alloys is faster at higher temperature, ~12 minutes at 150°C compared to ~24 minutes at 25°C. Nickel, of all metals and alloys, has the slowest kinetics at any particular temperature, and is followed by Fe-20Cr-Ni ternaries. The steady state passive corrosion is apparently lowered by the addition of Cr (actually replacement of Fe by Cr) to Fe-Ni alloys.

In the unsteady state period, the rate of decrease of current for Cr-containing alloys is slower at nobler potentials. Probably, this is due to slow rate of formation of passive film at nobler potentials. No significant trend is seen in Fe-Ni alloys. In one case, 80Fe-20Cr, the current at 150°C and -700 mV(SCE) did not steady in two hours, and instead, increased continuously. The potential -700 mV(SCE) corresponds to the peak potential of 80Fe-20Cr, and which implies an unstable passive film, causing the continuous corrosion. In the case of 95Fe-5Ni at 150°C and -800 mV(SCE) the current after a brief decay increased again before becoming steady. This again is probably due to changing nature of the passive film.

Fig. 17 - Pourbaix interpretation of anodic polarization behavior of pure metals in 19.5N NaOH at 25°C

Fig. 18 - Cathodic polarization behavior of Fe, Cr, and Ni in 19.5N NaOH at 25°C

Fig. 19 - Cathodic polarization behavior of Fe-Ni binaries in 19.5N NaOH at 25°C

Fig. 20 - Cathodic polarization behavior of Fe-20Cr-Ni alloys in 19.5N NaOH at 25°C

Fig. 21 - Cathodic polarization behavior of Fe, Cr, and Ni in 19.5N NaOH at 150°C

Fig. 22 - Cathodic polarization behavior of Fe-Ni binaries in 19.5N NaOH at 150°C

Fig. 23 - Cathodic polarization behavior of Fe-20Cr-Ni alloys in 19.5N NaOH at 150°C

Fig. 24 - Current vs. time behavior in passive region of Fe-Ni alloys in 19.5N NaOH at 25°C

Fig. 25 - Current vs. time behavior in passive region of Fe-20Cr-Ni alloys
in 19.5N NaOH at 25°C

Fig. 26 - Current vs. time behavior in passive region of Fe-Ni alloys in 19.5N NaOH at 150°C

Fig. 27 - Current vs. time behavior in passive region of Fe-20Cr-Ni alloys in 19.5N NaOH at 150°C

Fig. 28 - Corrosion rates of Fe-Cr-Ni alloys in 19.5N NaOH near passive peaks as a function of time

(b) 10N NaOH--Results of anodic and cathodic polarization in 10N NaOH at 118°C are given in Figs. 29 through 32. For results at lower temperatures and detailed discussion, see Reports COO-2018-18 (Q-5) and COO-2018-21 (Q-6).

4. Apparatus for Fused NaOH

(a) Cell (Autoclave) - An engineering drawing of the cell is given in COO-2018-(Q-7). Photographs of the cell are shown in Fig. 33. The 2-inch O.D. cylinders are made of nickel 270. The top and bottom plates are made of nickel 200 and the 1/4-inch O.D. pipes of nickel 201. All the nickel was supplied by International Nickel Company, Inc., Huntington Alloy Products Division.

Design of the cell allows for a separate electrochemical compartment for each electrode, i.e., working, reference, and counter electrode. It also allows for controlled atmosphere in each compartment through threaded holes in the top plate. The electrodes insulated in 1/8-inch O.D. alumina tubes will be positioned through respective electrode holders, as shown in Fig. 33.

(b) Crucible and instruments - The crucible, temperature controller, and the various instruments are shown in Fig. 34 and identified below:

- A. Easterline Angus Recorder, Type E1101S
- B. Tacussel Potentiostat, Type PRT 20-10X
- C. Keithley Electrometer, Model 600B
- D. Erwin Halstrup Motorpotentiometer MP165
- E. Lindberg Hevi-Duty Crucible Furnace, Model 56622A
- F. Lindberg Instrument Control Consul, Model 59344

Task 5 - Effect of Environment on Mechanistic Behavior (F. O. Du)

A. Aims

The aim of this work is to find the effects of environmental variables on the course of mechanistic processes associated with caustic SCC. This work emphasizes effects of environmental chemistry as opposed to Task 7 which emphasizes effects of metallurgical variables. This work also helps to interpret work in Task 6.

B. Results

1. Introduction

A detailed outline of the proposed experiments and associated apparatus is given in COO-2018-21 (Q-6). In this report results

Fig. 29 - Anodic polarization behavior of Fe-Ni binaries in 10N NaOH at 118°C

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Fig. 30 - Anodic polarization behavior of Fe-20Cr-Ni alloys in 10N NaOH in 118°C

Fig. 31 - Cathodic polarization behavior of Fe-Ni binaries in 10N NaOH at 118°C

Fig. 32 - Cathodic polarization behavior of Fe-20Cr-Ni alloys in 10N NaOH at 118°C

Cell and top plate with electrode holders

Cell with top plate in position

Fig. 33 - Nickel cell (Autoclave)

Fig. 34 - Apparatus for electrokinetic studies in fused sodium hydroxide.

of a few preliminary experiments with 304 stainless steel sheets stressed in U-form and immersed in fused NaOH are presented.

2. Experimental

(a) Specimens--Specimens, 3 inch x 1/2-inch size, were cut from as-received 10 mils thick 304 stainless steel sheets. The cut strips were then bent into a U-shape around an 1-inch diameter rod. The two ends of U-bent were joined, either by spot welding or holding with a small stainless steel clip, see Fig. 35. Maximum stresses in these U-bent specimens appropriately simulate stresses from cold worked tubings used for heat exchanger systems in a nuclear reactor.

(b) Fused NaOH crucible--High purity nickel crucible was used as container for the fused NaOH. The nickel crucible was placed inside a closed system, cylindrical zirconia crucible, where protective atmosphere can be established by argon purging. Figure 36 shows a photograph of the zirconium crucible. The zirconia crucible served also as a protection to the furnace in the event fused NaOH totally corroded the nickel container and leaked out. A second nickel crucible served as a holder or outside liner for the zirconia crucible in case fused NaOH spilled out from the zirconia crucible system. The crucible assembly was then placed in a Lindberg Hevi-Duty Crucible Furnace. A schematic diagram of the crucible assembly and the furnace is shown in Fig. 37.

A Lindberg Instrument Control Console Model 59344, designed especially to match the performance characteristic of the crucible furnace, was used to control the temperature to $\pm 1^\circ\text{C}$ accuracy. A sheathed alumel-chromel thermocouple immersed in the fused NaOH bath and connected to a potentiometer served as temperature monitor. The crucible assembly, furnace, controller, and the potentiometer are all shown in a photograph in Fig. 38. The furnace, etc., are placed in a hood to protect workers from fused NaOH fumes.

(c) Procedure--The test runs were made at 400° and 600°C with strained and strain-free samples, the latter serving as controls. In the first test specimens were immersed in a 400°C fused NaOH bath for 24 hours. In the second test specimens were immersed in a 600°C bath for three hours and left in the bath until the furnace cooled to room temperature. Specimens were then removed from the bath and cleaned with distilled water. Subsequently, the pencil scrubbing test on the adherency of the oxide scale and metallographic examination were performed. Nickel plating was necessary to prevent flaking of the oxides and rounding of the corners during polishing for metallographic examination.

Fig. 35 - U-bent specimens, nickel crucibles, and cylindrical zirconia crucible

Fig. 36 - Zirconia crucible with cover

Fig. 37 - Schematic diagram of the assembled crucible system and furnace

Fig. 38 - Photograph of test apparatus

3. Results

The U-bent specimens and undeformed specimens exposed at 400°C for 24 hours showed thick gray oxide scales on the surface, Fig. 39. The rubbing strokes of a pencil eraser did not produce peeling of the scales. Metallographic examination revealed only general type corrosion. No crack and intergranular type corrosion were observed.

The test at 600°C produced non-peeling gray oxide scales on the specimen's surface, similar to that at 400°C. However, metallographic examination revealed intergranular attack underneath the scales, near the region of maximum strain, Fig. 40. The attack is approximately one to two grains deep. The other regions of lesser strain showed only general corrosion and no intergranular attack. A photomicrograph of as-received stainless steel 304 is shown in Fig. 41 for comparison purposes.

Since only two investigations were made, the results are not conclusive that higher temperature and a critical strain simultaneously must exist to cause intergranular corrosion in fused NaOH. Both variables, bath temperature and stress level, produce sensitization and, thus, lead to intergranular attack.

Work suspended.

400°C

X500

Fig. 39 - Photomicrograph of stainless steel 304 specimen exposed to 400°C fused NaOH for 24 hours

600°C

X500

Fig. 40 Photomicrograph of stainless steel 304 specimen exposed to 600°C fused NaOH

X500

Fig. 41 - Photomicrograph of as-received stainless steel 304 specimen

Task 6 - The Straining Electrode and Transient Dissolution

A. Aims

In other work at OSU it has been shown that the straining electrode provides a good method for identifying those regions of electrochemical potential where SCC is most likely. The purpose of this task is to extend this understanding to caustic systems.

B. Results

Work suspended.

Task 7 - Initiation and Propagation of Cracks

A. Aims

The aim of this work is to study initiation and propagation processes in single crystals of Fe-Cr-Ni alloys. Special attention is to be paid to the crystallography of initiation and fracture processes. This work emphasizes metallurgical variables.

B. Results

Work suspended.

Task 8 - Corrosion Processes in Crevices

A. Aims

The aim of this work is to define electrochemical processes in crevices associated with caustic environments. Crevice effects include accelerated corrosion as well as the formation of insoluble corrosion products which expand and exert substantial forces. Both of these processes can be very destructive.

B. Results

Work suspended.

Task 9 - Dissolution at Grain Boundaries

A. Aims

Caustic SCC frequently occurs intergranularly and substantial intergranular attack is observed frequently when alloys are exposed to caustic environments. The purpose of this work is to define the amount and mechanism of intergranular corrosion and also that portion which is accelerated by stress.

B. Results

None this quarter.

Task 10 - Local Dissolution Processes on Caustic Environments (Paul Carter)

A. Aims

The aim of this work is to investigate initiation processes using thin foils which can be exposed to the environment, stressed, and subsequently examined in the electron microscope.

B. Results

1. Introduction

A schematic drawing, photographs of the apparatus, and experimental procedure are presented here. Results of a few preliminary runs are also reported.

2. Experimental

(a) Apparatus - A schematic drawing of the apparatus is shown in Fig. 42. Figure 43, photograph A, shows the side view of the fabricated apparatus, while photograph B shows the loaded specimens mounted on a rack and placed in front of the open furnace. The environment control chamber and specimen mounting rack are made of stainless steel. The furnace is a Thermodyne Type 6000 regulated with a Thermodyne Tacometer input controller. The event recorder is an Easterline Angus 20-pen recorder.

Humidity inside the environment chamber and furnace is controlled by blowing saturated hot air into the chamber.

(b) Specimens - The specimens used were cut from sheet metal strips 10 mils thick. All the metals were annealed at 1900-2000°F. Composition of the alloys is given in Table III and the dimensions of the specimen are shown in Fig. 44.

Fig. 42 - High temperature stress system.

Fig. 43 A - Assembled high temperature stress system - side view.

Fig. 43 B - Assembled high temperature stress system - mounted specimens.

Table III - Composition of Alloys

Metal	Nominal Composition, Wt. %					
	Cr	Ni	C	Mn	Si	Mo
S.S. 304	18.0-20.0	8.0-12.0	0.08 Max.	2.0 Max.	1.0	2.0-3.0
S.S. 316	16.0-18.0	10.0-14.0	0.08 Max.	2.0 Max.	1.0	
S.S. 430	14.0-18.0		0.12 Max.	1.0 Max.		
Incoloy-800	20.5 Fe 46.0	32.0 S 0.07	0.04 Max. Cu 0.30	0.75 Max.	0.35

Fig. 44 - Specimen

The surface of the specimens was cleaned prior to mounting by first grinding with 250-grit emery paper and then washing with acetone and distilled water.

(c). Experimental procedure - The following sequence of operations were followed for test runs.

1. The cleaned specimens were mounted on racks.
2. Predetermined weights were placed on them.
3. Electrical leads from the circuit recorder were connected to specimens.
4. The upper surface of the specimens were coated (swabbed) with one of the following three supersaturated solutions: NaCl, NaOH, or Na₂CO₃. The rack slid inside the furnace.

5. The furnace was raised to the desired temperature and humidity level.
6. Duration of the test run was recorded from circuit recorder.
7. The specimens were photomicrographed.

3. Results

Tables IV and V with Fig. 45 show the results of two preliminary test runs. None of the specimens failed in 16 days under the experimental conditions. The photomicrographs show intergranular and pitting corrosion.

Task 11 - Metallurgical Structure

A. Aims

The susceptibility of many alloys to SCC can be drastically altered by changing the metallurgical structure. Such changes can be effected by cold work precipitation hardening, special heat treatments and changes in alloy composition to produce certain phases. This work will consider possibilities for applying these procedures for preventing SCC.

B. Results

Work suspended.

Task 12 - Detailed Nature of the Passive Film

A. Aims

The aim of this task is to define the detailed aspects of chemistry and structure of the protective film on the surface of Fe-Cr-Ni alloys in caustic environments. This effect is important because all chemical reactions and stress corrosion cracking are related directly to the chemical or mechanical breakdown of these protective films.

B. Results

Work suspended.

Table IV - Test Run 1

Temp.: 450°C

Humidity: Inlet air saturated

Pen No.	Alloy	Solution Coating	Load on Specimens (gm)	Comment
1	I-800	NaOH	14	No failure in 16 days
2	↓			
3				
4				
5	↓			
6	304 S.S.			
7	↓			
8				
9	↓			
10				
11	430 S.S.			
12	↓			
13				
14	↓			
15				
16	316 S.S.			
17	↓			
18				
19				
20	↓			

Table V - Test Run 2

Temperature: 1100°C

Humidity: Not regulated

Pen No.	Alloy	Solution Coating	Load on Specimens (gm)	Comment
1	304 S.S.	Na ₂ CO ₃ + NaOH	23	No failure in 16 days
2		↓	39	
3		NaOH	12	
4		↓	6	
5		↓	6	
6		↓	6	
7		NaOH + NaCl	11	
8		↓	12	
9		↓	8	
10		Na ₂ CO ₃ + NaCl	18	
11			39	
12		↓	14	
13		Na ₂ CO ₃	11	
14		↓	14	
15		↓	20	
16		NaCl	39	
17		↓	6	
18			6	
19		↓	6	
20			35

(a) I-800

(c) SS 430

(b) SS 304

(d) SS 316

Fig. 45 - Photomicrographs of specimens (a) I-800, (b) SS 304, (c) SS 430, and (d) SS 316 exposed to humid environment under simulated IMFBR leak condition. Exposure time - 16 days; load - 14 gm; temperature - 450°C ; humidity - inlet air passed through boiling water; corrodent - NaOH. Photomagnification - 300X.

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