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STRESS CORROSION CRACKING OF FE-CR-NI ALLOYS
IN CAUSTIC ENVIRONMENTS

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January 15, 1970 - April 14, 1970

U. S. Atomic Energy Commission
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Argonne, Illinois

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REPORT

By

THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION

1314 KINNEAR RD.
COLUMBUS, OHIO 43212

To

U. S. ATOMIC ENERGY COMMISSION
Chicago Operations Office
9800 South Cass Avenue
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On

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

For the period January 15, 1970 - April 14, 1970

Submitted by

A. K. Agrawal and R. W. Staehle

Department of Metallurgical Engineering

Date February 23, 1971

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TABLE OF CONTENTS

<u>Section</u>		<u>Page</u>
1.0	ABSTRACT	1
2.0	CONCLUSIONS	1
3.0	INTRODUCTION	1
4.0	PROGRESS IN INDIVIDUAL TASKS	2
	Task 1 - Tests of Engineering Geometries	2
	Task 2 - General Effects of Alloy and Environmental Composition in Aqueous Solvents on Stress Corrosion Cracking (D. V. Subrahmanyam)	2
	Task 3 - General Effect of Alloy and Environmental Composition in Sodium Base Environments Containing NaOH on Stress Corrosion Cracking	27
	Task 4 - Dissolution and Passivation Behavior (K. G. Sheth)	27
	Task 5 - Effect of Environment on Mechanistic Behavior	53
	Task 6 - The Straining Electrode and Transient Dissolution	53
	Task 7 - Initiation and Propagation of Cracks	54
	Task 8 - Corrosion Processes in Crevices	54
	Task 9 - Dissolution at Grain Boundaries	54
	Task 10 - Local Dissolution Processes on Caustic Environments	55
	Task 11 - Metallurgical Structure	55
	Task 12 - Detailed Nature of the Passive Film	55
5.0	REFERENCES	56

1.0 ABSTRACT

Results from stress corrosion and electrochemical studies are reported for Fe-Cr-Ni alloys exposed to NaOH-H₂O solutions at temperatures below 200°C. Stress corrosion cracking of 304 stainless steel does not occur in boiling caustic solutions of 50% or lower concentrations. Pitting and transgranular type cracking occurs at only certain potentials. The electrochemical studies show that increasing temperature and/or caustic concentration causes more rapid dissolution of protective films on alloys. Replacement of Ni by Cr in Fe-Ni increases the corrosion rate several fold.

2.0 CONCLUSIONS

1. Stress corrosion cracking of 304 stainless steel has been investigated in various caustic solutions as a function of applied potentials. Pitting and transgranular cracking occurred in 50% NaOH only at potentials of -854, 146, and 246 mV_H. At other potentials specimens underwent either cathodic or anodic protection. (The most negative potentials correspond to deaerated solution and the high potentials tend to correspond to conditions of aeration.) At higher concentrations of NaOH both transgranular and intergranular type cracking occurred.

2. Polarization studies over a temperature range of 25-90°C and from 1-10N NaOH show that increasing the temperature and/or caustic concentration causes a drastic reduction in the passivity. It was confirmed that the replacement of Ni by either Cr or Fe in Fe-Cr-Ni alloys significantly accelerated the corrosion rates in the same solutions.

3.0 INTRODUCTION

This work is being conducted in support of the IMFBR 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 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

None this Quarter.

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

Preliminary results on the alloy chemistry in relation to caustic SCC in boiling 50 percent solution have been published in previous reports.^{1,2} Included also in these reports are the results of a few galvanostatically and potentiostatically controlled experiments on alloy 304 (18Cr-8Ni) and specially vacuum melted iron base alloys containing 11Ni-14Cr and 31Ni-13Cr.

During the current report period the effects of NaOH concentration under open-circuit conditions and the effect of applied potential on the caustic stress corrosion cracking of alloy 304 in boiling 50% NaOH have been investigated. The relevance of this line of study lies in the fact that caustic stress corrosion cracking phenomena depend on transient dissolution and passivation processes which are controlled by the applied potential. Different applied potentials in the anodic and cathodic regions can significantly alter the interfacial nature, interfacial reactions, and transport processes across the film.

The study of potential dependent cracking behavior is of recent origin and a few papers have appeared on mild steel in boiling hydroxide solutions.^{3,7} The controlled potential dictates the growth of different phases of oxides in the passive region via the formation of soluble HFeO_2^- anion. It is found that cracking occurs in a restricted range of potentials of about -600 to -1000 mV_H. These potentials agree very well with the potentials for formation of HFeO_2^- in the pH range 14-16. It is assumed that oxide films function in blocking the cracks. Cracking of iron or mild steel occurs in hydroxide solutions in the presence of Fe_3O_4 but not in the presence of Fe_2O_3 .

Studies of this type are extremely important for austenitic stainless steels. Once the kinetics and mechanism of caustic cracking are known, better methods of preventing cracking can be sought. This is the objective of the present study.

2. Experimental

Type 304 stainless steel wires (0.038 cm diameter) with a composition of 0.08C, 2.0Mn, 1.0Si, 0.065P, 0.035S, 18-20Cr, and 8-12Ni, and balance iron were vacuum annealed at 1200°C for two hours and air-cooled to avoid sensitization. Large grains could be developed by this procedure. The following aspects were studied on the behavior of this particular 304 stainless steel:

(a) Effects of NaOH concentration on failure times, crack morphologies, potential-time behavior, and polarization behavior. These studies were done in 20, 30, 50, 60, and 70% boiling solutions.

(b) In the potential range 246 to -954 mV_H, effects of applied potential on failure times, current-time curves, and crack morphologies: boiling 50% NaOH solutions were used for this study.

Details of specimen loading etc. are described in earlier reports.^{1,2} Polarization was carried out using a six-channel potentiostat, saturated calomel electrode as reference electrode, and platinum wire as counter electrode. The potentials were stepped up in 20-mV installments starting from the cathodic side and ending up in the transpassive region.

3. Results

(a) Effect of sodium hydroxide concentration on failure times and crack morphologies -- The effect of NaOH concentration on failure time at a stress equal to 100% Y.S. is shown in Fig. 1. Failure occurred in 60 and 70% NaOH solutions. Below these concentration failure did not occur. Failure times were lowered in the above solutions when the stress level was raised to 150% of Y.S.

The morphological features of the specimens exposed to various concentrations of boiling NaOH solutions without potentiostatic control are shown in Fig. 2. The following features are evident from the photomicrographs:

- (i) at 20 and 50% concentrations some intergranular and generalized corrosion occurred (a and b);
- (ii) in 60% NaOH solution, the unstressed specimen exhibited intergranular and general attack while the stressed specimens exhibited mixed type of failure at both the stress levels (i.e., 100 and 150% of yield stress), however, there is a predominance of transgranular character with crack branching (c-d);
- (iii) in 70% NaOH solution, the cracks are both intergranular and transgranular at stress levels of 100 and 150% of Y.S. (e and f).

(b) Effect of sodium hydroxide concentration on corrosion potentials and polarization curves -- The corrosion potentials shifted toward the active direction with increasing NaOH concentration, as shown in Fig. 3. The anodic dissolution kinetics is favored as the concentration is raised.

Figure 4 summarizes the potential-time curves in various boiling NaOH solutions. It can be noted that with time the stainless steel electrode was activated at all the concentrations except 60% NaOH. Initial passivation of the electrode occurred in 60% NaOH.

Figure 5 shows the potentiostatic polarization curves in 50 and 60% NaOH solutions. Curves 1 and 4 refer to the unstressed specimens in 50 and 60% NaOH solutions, respectively, while curves 2 and 3 refer to the stressed specimens in 50% solution.

The following regions are noticeable in 50% solution:

- (i) -1250 to -850 mV_H: cathodic region where hydrogen evolution or the film reduction process could be taking place;

Fig. 1 - Effect of sodium hydroxide concentration on failure times of 304 stainless steel

1000X

- a. 20% NaOH (boiling Pt. 112°C),
 $E_{\text{corr}} = -94 \text{ mV}_H$, Load: 100% Y.S.
 Not failed in 15 days

1000X

- b. 50% NaOH (boiling Pt. 125°C),
 $E_{\text{corr}} = -464 \text{ mV}_H$, Load: 100% Y.S.
 Not failed in 15 days

500X

- c. 60% NaOH (boiling Pt. 140°C),
 $E_{\text{corr}} = -924 \text{ mV}_H$. Unstressed

Fig. 2 - Photomicrographs of 304 stainless steel exposed to various concentrations of boiling NaOH solutions without any potentiostatic control

200X

- d. 60% NaOH (boiling Pt. 140°C),
 $E_{corr} = -924 \text{ mV}_H$, Load: 100% Y.S.
 $T_f = 102 \text{ hr.}$

150X

- e. 60% NaOH (boiling Pt. 140°C),
 $E_{corr} = -924 \text{ mV}_H$, Load: 150% Y.S.
 $T_f = 65.5 \text{ hr.}$

Fig. 2 - continued

f. 70% NaOH (boiling Pt. 148°C),
 $E_{\text{corr}} = -954 \text{ mV}_H$, Load: 100% Y.S.
 $T_f = 44 \text{ hr.}$

g. 70% NaOH (boiling Pt. 148°C),
 $E_{\text{corr}} = -954 \text{ mV}_H$, Load: 150% Y.S.
 $T_f = 36 \text{ hr.}$

Fig. 2 - continued

Fig. 3 - The effect of sodium hydroxide concentration on corrosion potential of stressed 304 stainless steel

Fig. 4 - Potential-time curves for 304 stainless steel as a function of hydroxide concentration

Fig. 5 - Potentiostatic polarization curves for 304 stainless steel in 50% and 60% sodium hydroxide solutions

- (ii) -780 to -700 mV_H: a short anodic region with a peak at -720 mV;
- (iii) -680 to -350 mV_H: cathodic region in which very weak cathodic currents are flowing;
- (iv) -350 to -110 mV_H: in this region tafel behavior is observed with a slope of 70 mV; and
- (v) -100 to +240 mV_H: transpassive region below oxygen evolution potential.

In 60% NaOH solution it can be noticed that the relative magnitudes of the cathodic and anodic currents are increased. The first anodic peak is shifted by 130 mV, while the second one in transpassive region is shifted by 50 mV in the negative direction. There exists a tafel slope of 70 mV in the region -300 to -150 mV_H and this is similar to that observed in 50% hydroxide solution, in region (iv).

Tafel behavior has not been observed in the above solutions in the cathodic region.

(c) Effect of potential on failure times -- Figure 6 shows the effect of potential on the failure times in the range of potentials +254 to -954 mV_H. Failure occurred at 246 and 146 mV_H in the anodic range and at -854 mV_H in the cathodic range. At other potentials there was no failure.

(d) Effect of potential on crack morphologies -- Figure 7 shows the photomicrographs of alloy 304 exposed in 50% boiling NaOH solutions at different constant potentials in the range 246 to -954 mV_H.

At very positive potentials, namely 246 and 146 mV_H the failure appears to have taken place by pitting (photos b and c). The same pitting features can be seen in the unstressed specimen also at 246 mV_H (photo a). As the potential is made more negative the pitting mode of attack changes into a generalized type of attack without failures or any evidence of stress corrosion cracks, as shown in photos d-h. This type of morphology can be seen in the potential range 46 to -754 mV_H. However, at -854 mV_H, the failed specimen indicated some evidence of transgranular cracks (photo i). At -954 mV_H, both the unstressed and stressed specimens indicate no evidence of either stress corrosion or generalized attack (photos j and k).

(e) Current-time curves at different potential -- The generalized trend on the effect of stressing is indicated by curves 2 and 3 in Fig. 5. Curve 2 was plotted from the values measured immediately after stressing, and curve 3 was plotted from the values measured after a period of 2 to 15 days depending on the failure time. When compared to the unstressed curve 1, there is a lowering of the cathodic kinetics in the cathodic region. This indicates that stressing

Fig. 6 - Effect of potential on failure times of 304 stainless steel

a. 246 mV_H
Unstressed

500X

b. 246 mV_H
T_F = 12 hr

500X

c. 146 mV_H
T_F = 24 hr

200X

Fig. 7 - Photomicrographs of 304 stainless steel exposed to boiling 50% sodium hydroxide solutions at various constant potentials Load: 100% Y.S.

d. 46 mV_H
Not failed in 15 days

500X

e. -254 mV_H
Unstressed

500X

f. -254 mV_H
No failure in 15 days

500X

Fig. 7 - continued

g. -354 mV_H
No failure in 15 days

1000X

h. -754 mV_H
No failure in 15 days

i. -854 mV_H
 $T_f = 133 \text{ hr}$

300X

Fig. 7 - continued

j. -954 mV_H
Unstressed

200X

k. -954 mV_H
No failure in 15 days

200X

Fig. 7 - continued

kinetics in the cathodic region. This indicates that stressing accelerates the anodic kinetics in cathodic potential region. The currents still remained in the cathodic region. Comparison of curves 2' and 3' with 1' in the anodic region indicates a lowering of the anodic kinetics upon stressing the specimens.

However, comparison of curve 2 with 3 and 2' with 3' clearly indicates time-dependent changes in the cathodic and anodic processes in this system. These changes of current with time are plotted at different potentials in Figs. 8-11. To avoid overlapping, they are plotted separately at 246, -254, and -954 mV_H; the currents for unstressed and stressed specimens are compared below.

Potential (mV _H)	Current, i (A x 10 ⁵)	
	unstressed	stressed
246	5	1.8
-254	9	0.64
-954	-7	-5.2

The observed differences in currents for unstressed and stressed specimens could be due to the reduction in the area of the specimen and consequent changes in rates of passivation or active dissolution.

- (i) At potentials -954 mV_H and -754 mV_H the curves remained in the cathodic region with a tendency to pass to the anodic region at -754 mV_H. However, at -854 mV_H an anodic transient can be noticed with a peak current of 10⁻³A. This value happens to be on the anodic peak in the polarization curves in Fig. 5. Failure took place at this potential (Fig. 8).
- (ii) At potentials -654, -554, -454, and -354 mV_H the curves consisted of a series of dissolution and passivation events except at -654 mV_H, in which constant cathodic currents are observed. This potential value gave rise to cathodic currents on unstressed specimens (Fig. 9).
- (iii) At potentials -254, -154, and -54 mV_H anodic currents are observed (Fig. 10). It can be notified that at potentials -154 and -54 mV_H the curves indicated the possibility of anodization → pitting → repassivation. At these potentials, failure did not take place. A similar trend is observed at 46 mV_H also. However, at potentials 146 and 246 mV_H the

Fig. 8 - Current-time curves for 304 stainless steel at -954, -854 and -754 mV_H

Fig. 9 - Current-time curves for 304 stainless steel at -654, -554, -454 and -354 mV_H

Fig. 10 - Current-time curves for 304 stainless steel at -254, -154, and -54 mV_H

Fig. 11 - Current-time curves for 304 stainless steel at 46, 146, and 246 mV_H

curves did not indicate repassivation transients, indicating that the pits do not repassivate and that the anodization and pitting might have taken place in a very short period of time; i.e., less than a minute (Fig. 11).

To summarize, in the cases where the currents remained in the cathodic region or where the curves showed a significant tendency to repassivate, the failure did not take place. Also, these features are confirmed in the morphological features.

4. Discussion

It has been observed that cracking occurs in boiling NaOH solutions above 50% concentration. If total failure has to occur in concentrations below 50% caustic, the stress level has to be higher than 100% Y.S. The morphological features at low concentrations prove that either once the stress is above 100%, or the temperature is raised above boiling point under pressure (for instance in autoclaves) total failure occurs.

It was noticed that failures occur at positive potentials of 246 and 146 mV_H which are below the oxygen evolution potential and, also, at a quite negative potential of -854 mV_H.

The observed trends in cracking dependence on NaOH concentration and potential can be explained by using the Pourbaix potential-pH diagrams for iron, nickel, and chromium. Under the conditions of study, where pH was in the range 14.4 - 15.3 (10 - 70% NaOH) the formation of HFeO_2^- , HNiO_2^- , and CrO_3^- ions (dihydroferrite, dihydronicelate and chromite, respectively) can take place. Various reactions occurring at pH 15.1 (50% NaOH) over iron, nickel, and chromium and the equilibrium potentials E_0 are as follows*:

(1) Reactions with Fe (formation of HFeO_2^- ion):

$$\begin{aligned} \text{Fe} + 2\text{H}_2\text{O} &\rightleftharpoons \text{HFeO}_2^- + 3\text{H}^+ + 2\text{e} \\ E_0 &= 0.493 - \frac{3}{2} \cdot \frac{RT}{F} \cdot (\text{pH}) + \frac{RT}{2F} \log [\text{HFeO}_2^-] \\ &= 0.493 - \frac{3}{2} \cdot (0.07943 \times 15.1) + \frac{1}{2} \cdot 0.07943 \times (-6) \\ &= 0.493 - 1.775 - 0.238 = -1.25\text{V} \end{aligned} \quad (1)$$

*In all the cases equilibrium concentrations of 10^{-6}N , HFeO_2^- , HNiO_2^- and CrO_3^- have been assumed.

$$E_0 = -0.085 - \frac{RT}{F} [\text{pH}] \quad (2)$$

$$E_0 = -0.085 - 0.07943 \times 15.1 = -0.085 - 1.182 = -1.276\text{V}$$

$$\begin{aligned} E_0 &= -1.819 + \frac{RT}{2F} [\text{pH}] - \frac{3}{2} \cdot \frac{RT}{F} \log [\text{HFeO}_2^-] \\ &= -1.819 + (0.03976 \times 15.1) - (1.5 \times 0.07943 \times -6) \\ &= -1.819 + 0.6 + 0.715 = -0.504\text{V} \end{aligned} \quad (3)$$

$$E_0 = 1.208 - \frac{RT}{F} \text{pH} = 1.208 - 1.200 = 0.008 \text{ mV} \quad (4)$$

(ii) Reactions with Ni (formation of HNiO_2^- ion):

$$\begin{aligned} E_0 &= 0.648 - \frac{3}{2} \frac{RT}{F} [\text{pH}] + \frac{RT}{2F} \log [\text{HNiO}_2^-] \\ &= 0.648 - 1.775 - 0.238 = -1.365\text{V} \end{aligned} \quad (1)$$

$$\begin{aligned} E_0 &= -0.718 + \frac{RT}{2F} [\text{pH}] - \frac{3}{2} \cdot \frac{RT}{F} \log [\text{HNiO}_2^-] \\ &= -0.718 + 0.6 + 0.718 = +0.570\text{V} \end{aligned} \quad (2)$$

(iii) Reactions with Cr (assuming the formation of CrO_3^{--}):

$$\begin{aligned} E_0 &= 0.374 - \frac{1}{5} \frac{RT}{F} [\text{pH}] + \frac{1}{3} \log \frac{RT}{F} [\text{CrO}_3^{--}] \\ &= 0.0374 - \frac{1}{5} \times (0.07943 \times 15.1) + \frac{1}{3} \times (0.07943) \log (10^{-6}) \end{aligned} \quad (1)$$

(assuming the formation of 10^{-6} ions of CrO_3^{--} at -Ve potentials)

$$= 0.0374 - 0.24 + 0.159 = -0.044\text{V}$$

From the foregoing, it can be seen that in 10% boiling NaOH with a pH of 14.4 and boiling point of 110°C the corrosion potential is -64 mV_H. The equilibrium potential for the reaction $2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} = 3\text{Fe}_2\text{O}_3 + 2\text{H}^+ + 2\text{e}$ calculated under the above conditions is -101 mV_H. The observed value suggests the formation of protective Fe_2O_3 and HfNiO_2^- and CrO_3^{--} ions. Hence the cracking does not take place.

In 50% NaOH the observed corrosion potential -464 mV_H coincides with the equilibrium potential for $3\text{HfFeO}_2^- + \text{H}^+ = \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + 2\text{e}$. Yet the cracking did not occur but showed some intergranular and transgranular cracks. This shows that stress is insufficient to cause total failure at 100% Y.S. (cracking was observed at 150% Y.S.). At this potential an equilibrium between $\text{HfFeO}_2^-/\text{Fe}_3\text{O}_4$ and $\text{HfNiO}_2^-/\text{Ni}_3\text{O}_4$ exists.

In 70% NaOH, where pH is 15.3 and the boiling point is 148°C , this alloy exhibited a corrosion potential of -954 mV_H. This value is close to the value of -1365 mV_H for $\text{Fe}/\text{Fe}_3\text{O}_4$ equilibrium. Cracking was observed in concentrations lower than this; e.g., 60% NaOH of pH 15.2 where the corrosion potential of almost the same magnitude was observed.

Under the above potentials, Ni and Cr remain as HfNiO_2^- and CrO_3^{--} , respectively. Being predominately iron base alloy, it is reasonable to base the observations on oxidation schemes of water and iron in the entire system. Nickel functions to inhibit the oxidation of Fe. This agrees with observations in the literature where cracking of pure iron was found at temperatures below the boiling point and concentrations below 50% NaOH.

However, to base the entire effects on concentration may be rather erroneous. The reason is that boiling point increases with increase in NaOH concentration, thereby raising the RT/F value. Therefore, further work is essential to determine the temperature effects at

each concentration. In the published literature potentiostatic polarization curves in strong alkalis have not been treated from the kinetic point of view.

Different branches observed in the potentiostatic polarization curves in Fig. 5 can be summarized as follows:

- (i) in the cathodic region the hydrogen evolution takes place where the tafel slopes were not observed ($H^+ + e \rightarrow 1/2 H_2$);
- (ii) in the anodic region, the following sequence of events take place:
 $Fe \rightarrow HFeO_2^- \rightarrow Fe_3O_4 \rightarrow Fe_2O_3$
 $Ni \rightarrow HNiO_2^- \rightarrow Ni_3O_4$
 $Cr \rightarrow CrO_3^- \rightarrow Cr_2O_3$
- (iii) the observed tafel slopes in 50 and 60% hydroxide solutions correspond to the oxidation scheme $HMO_2^- \rightarrow M_3O_4$ where M stands for Fe and Ni.

It can also be noted that because of the probable rapid oxidation of HMO_2^- anions there is a reduction in the anodic tafel region as the concentration is raised to 60%. Oxidation to oxides is complete within a very narrow range of potentials, and a transpassive dissolution range is reached at -154 mV_H and -204 mV_H in 50 and 60% NaOH, respectively. The probable oxides are Fe_2O_3 , Ni_3O_4 , and Cr_2O_3 .

There is a clear correlation between the crack morphologies, current-time curves, and various regimes in the polarization curve for 50% NaOH solutions. Cracking and total failure occurs in the transpassive dissolution range 246 to 46 mV_H attended by pitting. The wiggles in the current-time curves relate to the activation and repassivation of pits and cracks. Severe intergranular corrosion occurs in the active dissolution range without cracking or total failure. At -854 mV_H the failure could be due to the rapid formation of $HFeO_2^-$ and $HNiO_2^-$ and lack of passivation. At -954 mV_H the stress corrosion cracking, intergranular corrosion is completely prevented. This emphasizes the importance of cathodic protection potential in the prevention of intergranular SCC. For carbon steels, cathodic protection prevented intergranular SCC of mild steel in black liquors or sulfuric acid solutions.

With these results in mind, future studies will be carried out as follows:

- (i) Potential dependent cracking of 304 stainless steel as a function of NaOH concentration and temperature.

- (ii) Effects of applied potential on different Fe-Ni-Cr alloys at various NaOH concentrations and temperatures.
- (iii) Activation and repassivation of cracked oxides of 304 in NaOH solutions upon instantaneous straining which gives an insight into the transient processes as governing factors in caustic stress corrosion cracking.

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 take in Task 2 except for the environment being a sodium base.

B. Results

None this Quarter.

Task 4 - Dissolution and Passivation Behavior (K. G. Sheth)

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 occurs 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

The present work is to investigate the effects of temperature, pH, and alloy concentration on the polarization behavior of Fe-Ni and (Fe + 20Cr) - Ni alloys. Compositions of various alloys used for this investigation are given in a previous report.² These alloys were selected with a view in mind to study the effect of nickel in Fe-Ni.

The corrodent or the electrolyte used for these investigations was 1, 5, and 10 N NaOH. Temperatures studied were in the range 25-90°C.

2. Experimental

The experimental setup was similar to that described elsewhere.¹ One change was that the X-Y recorder was replaced with a microamp strip chart recorder whose chart speed was constant at 6 inches/hr, and thus, length of the chart recorded gave a measure of the increasing potential. Anodic polarization was done potentiodynamically at a constant rate of 600 mV/hr, starting at steady state corrosion potential of the sample. All potentials referred to in this section were measured against a saturated calomel electrode (SCE) which was at room temperature (~25°C).

3. Results

The corrosion potentials of alloys 2, 3, 4, 12, 51, 55, 58, and 62 in various caustic solutions at 70°C are given in Table I, and corrosion potentials in 10N caustic solution at various temperatures are given in Table II. The anodic polarization curves of these alloys are shown in Figs. 12 to 33. These figures are arranged together in groups to facilitate an understanding of the effects of composition, solution concentration, and temperature. Figures 12 to 17 show the effect of nickel addition on the anodic behavior of Fe-Ni binary and Fe-20Cr-Ni ternary alloys in different caustic solutions. Figures 18 to 25 show the effect of increasing temperature, and Figs. 26 to 33 show the effect of increasing caustic concentration on the alloys. Tafel slopes in the transpassive region (i.e., oxygen evolution region) obtained from the polarization curves are listed in Tables III and IV as a function of concentration and temperature, respectively. This newly acquired set of data confirms the observations made from the limited amount of work reported in COO-2018-11(Q-4).

Results shown in Table I and II indicate that increasing the nickel content in both binary and ternary alloys, except in alloy #2, shifts the corrosion potentials to slightly more noble values. For almost all alloys an increase in caustic concentration and temperature is found to shift their corrosion potentials to the active side. The shifts are more pronounced in Fe-Ni binaries than in other alloys.

From Figs. 12 to 17 it can be observed that replacing nickel with chromium in the Fe-Ni binary considerably increases its corrosion rate (approximately tenfold), especially in high caustic concentration. The effect of replacing nickel with iron in the ternary is similar in strong caustic. This is found to be in fair agreement with Pourbaix diagrams showing the comparatively high solubility of chromium oxides compared to nickel oxides in high potential-pH regions. Addition of nickel brings the oxygen evolution potential to a slightly more active side and, consequently, at any potential in the transpassive

Table I - Corrosion Potentials in
Various Caustic Solutions
at 70°C

Alloy No.	E _{corr} , V(SCE)		
	Caustic Concentration		
	1N	5N	10N
2			-1.10
3	-0.315		-1.10
4	-0.215		-0.980
12	-0.290	-0.335	-0.435
51	-0.380	-0.380	-0.485
55	-0.300	-0.340	-0.485
58	-0.260	-0.360	-0.410
62	-0.250	-0.520	-0.870

Table II - Corrosion Potentials at Various
Temperatures in 10N NaOH

Alloy No.	E _{corr} , V(SCE)			
	Temperature (°C)			
	25	50	70	90
2	-0.360	-0.490	-1.10	-1.12
3	-0.830	-1.06	-1.10	-1.11
4	-0.560	-0.975	-0.980	-0.990
12	-0.430	-0.350	-0.435	-0.350
51	-0.590	-0.540	-0.485	
55	-0.460	-0.490	-0.485	-0.450
58	-0.320	-0.360	-0.410	-0.450
62	-0.760	-0.830	-0.870	-0.870

Fig. 12 - Anodic polarization behavior in 1N NaOH at 70°C

Fig. 13 - Anodic polarization behavior in 1N NaOH at 70°C

Fig. 14 - Anodic polarization behavior in 5N NaOH at 70°C

Fig. 15 - Anodic polarization behavior in 5N NaOH at 70°C

Fig. 16 - Anodic polarization behavior in 10N NaOH at 70°C

Fig. 17 - Anodic polarization behavior in 10N NaOH at 70°C

Fig. 18 - Effect of temperature on anodic polarization behavior of alloy #2 in 10N NaOH

Fig. 19 - Effect of temperature on anodic polarization behavior of alloy #3 in 10N NaOH

Fig. 20 - Effect of temperature on anodic polarization behavior of alloy #4 in 10N NaOH

Fig. 21 - Effect of temperature on anodic polarization behavior of alloy #12 in 1N NaOH.

Fig. 22 - Effect of temperature on anodic polarization behavior of alloy #51 in 10N NaOH

Fig. 23 - Effect of temperature on anodic polarization behavior of alloy #55 in 10N NaOH

Fig. 24 - Effect of temperature on anodic polarization behavior of alloy #58 in 1N NaOH

Fig. 25 - Effect of temperature on anodic polarization behavior of alloy #62 in 10N NaOH

Fig. 26 - Effect of caustic concentration on anodic polarization behavior of alloy #2 at 70°C

Fig. 27 - Effect of caustic concentration on anodic polarization behavior of alloy #3 at 70°C

Fig. 28 - Effect of caustic concentration on anodic polarization behavior of alloy #4 at 70°C

Fig. 29 - Effect of caustic concentration on anodic polarization behavior of alloy #12 at 70°C

Fig. 30 - Effect of caustic concentration on anodic polarization behavior of alloy #51 at 70°C

Fig. 31 - Effect of caustic concentration on anodic polarization behavior of alloy #55 at 70°C

Fig. 32 - Effect of caustic concentration on anodic polarization behavior of alloy #58 at 70°C

Fig. 33 - Effect of caustic concentration on anodic polarization behavior of alloy #62 at 70°C

Table III - Tafel Slopes in Transpassive Region
in Various Caustic Solutions at 70°C

Alloy No.	Slope, b (mV)		
	Caustic Concentration		
	1N	5N	10N
2	50	45	40
3	35	45	50
4	40	37	50
12	50	50	55
51	40	37	37
55		45	45
58	50	50	50
62	50	45	70

Table IV - Tafel Slopes in Transpassive Region at
Various Temperatures in 10N NaOH

Alloy No.	Slope, b (mV)			
	Temperature (°C)			
	25	50	70	90
2	45	45	40	50
3	50	50	50	50
4	45	45	50	55
12	50	55	55	
51			37	
55	50	45	45	50
58	50	50	50	60
62	62	55	70	60

region the rate of oxygen evolution is higher in nickel-rich alloys.

The effects of caustic concentration and temperature were nearly identical. An increase in temperature, as would be expected, enhanced the reaction rates through the entire potential range (see Figs. 18 to 25), whereas strong caustic probably destroyed the protective film on the alloys and, thereby brought them in active dissolution region (see Figs. 26 to 33). At low temperatures and solution concentrations the active dissolution peaks of Fe-Ni binaries are absent from polarization curves because their corrosion potentials are in the passive region. However, these peaks can be observed in polarization curves done at higher temperatures and caustic concentrations. In the case of ternaries, active peaks became more distinct with a rise in temperature and concentrations.

The oxygen evolution potentials were also lowered (made less noble) in both circumstances; i.e., with temperature or concentration, or both. Tafel slopes for oxygen evolution in Tables III and IV lie in the range 35-60 mV and are found to be independent of temperature, caustic concentration, and alloy composition. These values are in fair agreement with those reported by Tsinman;⁸ i.e., 45-49 mV for pure iron in alkaline solutions. Hence, the oxygen evolution mechanism proposed by him for pure iron may be applicable to those alloys also.

Task 5 - Effect of Environment on Mechanistic Behavior

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 on 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

None this Quarter.

Task 6 - The Straining Electrode and Transient Dissolution

A. Aims

In other works 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

None this Quarter.

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

None this Quarter.

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

None this Quarter

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

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

None this Quarter.

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

None this Quarter.

Task 12 - Detailed Nature of the Passive Film

A. Aims

The aim of this task is to define the detailed aspect 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

None this Quarter.

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