Corrosion, Stress Corrosion Cracking, and
Electrochemistry of the Iron and Nickel Base
Alloys in Caustic Environments

R. W. Staehle
Professor

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

A. K. Agrawal
Adjunct Assistant Professor

490 3000

Department of Metallurgical Engineering
The Ohio State University
Columbus, Ohio

Progress Report for the Period
1 March 1978 to 28 February 1979

United States
Energy Research and Development Administration

Contract No. EY-76-S-02-2421. A002

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

1.0 ABSTRACT

Stress corrosion cracking susceptibility of 2-1/4Cr-1Mo steel has been studied in the pH range 0.5 to 13 in one molar sulfate solutions containing Na_2S additions, by the slow strain rate (10^{-6}s^{-1}) technique. Brittle fracture was observed over the entire pH range but only at cathodic potentials which were below the hydrogen evolution region. Fractures at cathodic potentials were probably due to the hydrogen embrittlement which was accentuated by the sulfide present in the environment. At anodic potentials failures in straining tests were due to either general corrosion or mechanical ductile fracture.

Crack propagation rates (CPRs) in Nickel-200 have been measured as a function of potential in 17.5N NaOH solution at 138°C , using the fast straining electrode technique. CPRs in the potential range -0.75 to $-0.6V_{\text{H}}$ were found to be high on the order of 10^{-8}m/s , but relatively low $<10^{-9}\text{m/s}$, outside this potential range. It was deduced that the high nickel alloys, e.g., Inconel-600, in the active potential range -0.75 to $-0.6V_{\text{H}}$ will have high CPR in caustic solutions due to the high reactivity of nickel.

Crack propagation rates of Type 304L at 138°C in 17.5N NaOH solution with and without a chromate inhibitor have been measured as a function of potential using the fast straining electrode technique. No significant drop in the CPR was observed due to the presence of the inhibitor in the solution. Therefore, it was concluded that $\text{CrO}_4^{=}$ ions, though very effective in preventing stress corrosion cracking in Type 304 under static load conditions, will not be beneficial under transient conditions, such as cyclic stressing which would cause repeated breakdown of the protective film.

Corrosion rates of pure metals Fe, Cr, and Ni have been estimated as a function of potential in the 17.5N NaOH solution at 130°C using the long-time current decay measurements. Of the above three metals, iron was found to be most unstable in the caustic solution over the entire potential range from -1.0 to 0.4V_H. The current in this potential range, even after 1000 minutes exposure, was on the order of 10⁻³A/cm², which is equivalent to a corrosion rate greater than 1 cm/year. On the other hand, the current for chromium at potentials below -0.3V_H was less than 10⁻⁶A/cm², indicating a negligible corrosion rate. However, at oxidizing potentials above -0.3V_H, the current increased and at -0.1V_H was higher than that for Fe. Nickel showed intermediate behavior between Fe and Cr. The current for Ni was on the order of 10⁻⁵A/cm² between -0.75 and -0.6V_H, and near 0.0V_H. At other potentials the current was even less. Passivation of Cr, like Ni, occurs after an incubation time, after which the film grows by a place-exchange mechanism.

The double layer capacitance of Fe, Ni, and Cr in 17.5N NaOH has also been measured using a potential stepping technique.

TABLE OF CONTENTS

	<u>Page</u>
1.0 ABSTRACT	i
2.0 INTRODUCTION	1
3.0 PROGRESS IN INDIVIDUAL TASKS	
Task 1 - Fundamental Measurements of Stress Corrosion Cracking Parameters of Ferritic Steels in Aqueous Sulfide Environments	2
Task 2 - Fundamental Electrochemical and Corrosion Studies of Pure Iron and Selected Alloys in Aqueous Sulfide Environments	16
Task 3 - Fundamental Measurements of Stress Corrosion Cracking Parameters, Including Inhibitors in the Caustic Environment	17
Task 4 - Fundamental Electrochemical and Corrosion Studies of Pure Metals Fe, Cr, and Ni in the Caustic Environment	31
4.0 APPENDIX A	
"The Stress Corrosion Cracking Behavior of Type 304 Stainless Steel in Boiling 50% NaOH Solution"	44

2.0 INTRODUCTION

The work accomplished and the activities related to the project "Corrosion, Stress Corrosion Cracking, and Electrochemistry of the Iron and Nickel Base Alloys in Caustic Environments" during the current reporting period of 1 March 1978 to 28 February 1979 are reported here. This project is carried out under the U.S. DOE Contract No. EY-76-S-02-2421. A002.

Progress in various Tasks are described in Section 3.0 under their individual task headings. Other related activities are described below.

During the current reporting period three technical papers were presented in various society meetings.

1. "The Electrochemistry and Corrosion of Iron in Sulfide-Containing Solutions," S.A. Bradford, A.K. Agrawal, and R.W. Staehle at the 153rd Electrochemical Society Meeting, Seattle, Washington, May 21-26, 1978.
2. "Oxidizing Anions as Inhibitors," A.K. Agrawal at the Gordon Research Conference on Corrosion, New London, New Hampshire, July 10-14, 1978.
3. "The Stress Corrosion Cracking Behavior of Type 304 Stainless Steel in Boiling 50% NaOH Solution," D.V. Subrahmanyam, A.K. Agrawal, and R.W. Staehle at the 7th International Congress on Metallic Corrosion, Rio de Janeiro, Brazil, October 4-11, 1978.

The papers were presented by the underlined authors. The third paper above has been submitted for publication in the Proceedings of the 7th International Congress on Metallic Corrosion. The paper is included in this report as Appendix A.

TASK 1

Fundamental Measurements of Stress Corrosion Cracking Parameters of Ferritic Steels in Aqueous Sulfide Environments

S. Bradford*, A.K. Agrawal, and R.W. Staehle

INTRODUCTION

The general objective of this task is to investigate the stress corrosion cracking susceptibility of molybdenum containing ferritic (Fe-Cr-Mo) steels in aqueous environments containing sulfide. Thermodynamically the sulfide specie is stable as dissolved H_2S in acidic pH range, as HS^- ions in alkaline pH's, and as $S^{=}$ ions in strongly alkaline solutions. In the present study the stress corrosion cracking susceptibility of 2-1/4Cr-1Mo steel has been investigated over a wide range of pH in the presence of sulfide in 1M Na_2SO_4 solutions. Stress corrosion cracking tests were run at anodic and cathodic controlled potentials in order to simulate the oxidizing and the reducing environments. The slow strain rate technique was used for the stress corrosion cracking tests.

EXPERIMENTAL

Test specimens. The as-received hot rolled 2-1/4Cr-1Mo steel was in the form of rectangular bars, having a Rockwell hardness of R_A 32. The

* Present address: Department of Mineral Engineering, The University of Alberta, Edmonton, Canada.

chemical analysis of the steel supplied by the vendor was

<u>C</u>	<u>Mn</u>	<u>Cr</u>	<u>Si</u>	<u>Mo</u>	<u>S</u>	<u>P</u>	<u>Cu</u>
0.12	0.46	2.36	0.37	0.99	0.013	0.008	0.10%

The bars were swaged, in several stages, to 0.62 cm diameter rods, which were then cut into 23 cm lengths for test specimens. The swaged rods had a hardness of R_A 52. Rods were machined to 0.25 cm diameter in the gage section, which was 1.25 cm in length at the center of the 23 cm rod.

The machined specimens were cleaned with acetone and distilled water then encapsulated in evacuated quartz tubes, and annealed for one hour at 900°C and furnace cooled. The annealed specimen had a hardness of R_A 20 and a microstructure showing a ferritic matrix with carbide clusters.

Any tarnish on the gage section of a specimen was polished off with one-micron chromic oxide paste. The specimens were then thoroughly washed with distilled water and cleaned with acetone. The unreduced sections of the specimens were covered with shrinkable Teflon tubing, leaving only the gage section exposed.

Solutions. The test environment was essentially 1M Na_2SO_4 solution whose pH was adjusted to the desired value between 0.5 to 13 with either H_2SO_4 or NaOH. For the 0.5 pH only H_2SO_4 was used for making the solution. The test solution was deaerated with purified argon prior to adding concentrated Na_2S solution to give a sulfide concentration of 30 or 100 ppm. The Na_2S addition was made in the Teflon test cell, described below.

Apparatus. The slow-strain rate machine with the Teflon cell used in the stress corrosion cracking tests is shown in Figure 1. The electrolytic cell was made of Teflon with internal dimensions 7.7 cm in diameter and 8.3 cm high. Teflon gas-tight fittings are provided (only a few are

Figure 1. The slow strain rate machine with the Teflon cell.

shown in the Figure) to allow the test specimen to extend out the top and bottom of the cell, to allow entrance of a Luggin probe and drain tube through the bottom, and a gas inlet, gas outlet, and a mercury thermometer through the top. Also, extending through a fitting in the cell top is the platinum counter electrode made of 0.75 mm wire spot-welded into circular grid 7 cm in diameter and 5 cm high.

The Luggin probe was connected through a closed, wetted stopcock to a $\text{Hg/Hg}_2\text{SO}_4$ reference electrode in a saturated K_2SO_4 solution. The drain tube at the bottom is connected to a solenoid valve that is normally closed. A proximity switch on the load vs. time chart recorder is set to activate when the specimen fractures, shutting off power to all the instruments while opening the solenoid drain valve.

A Wenking Model 68TS3 potentiostat was used for controlling the potential. Two Esterline Angus recorders were used, one for monitoring the current and the other for load transmitted by the load-cell on the straining machine.

The slow-strain rate machine is powered by a 1/8th h.p., 1800 rpm, single-phase electric motor geared to produce nominal strain rates of $5 \times 10^{-7} \text{ s}^{-1}$, $2.5 \times 10^{-6} \text{ s}^{-1}$, or $1.25 \times 10^{-5} \text{ s}^{-1}$ in a specimen with 1.25 cm gage length. All the tests reported here were made at the middle rate.

Procedure. After a specimen was mounted in the cell on the straining machine, the cell was filled with the test solution and degassed with Argon. A desired amount of Na_2S was added to the solution when the degassing was complete. A potential was applied, and the slack on the specimen was removed before starting the straining. Fractured specimens were removed from the cell and examined under an SEM. A few reference tests were also made in argon, without any solution, for comparison purposes.

The time vs. load curve was used to calculate the total elongation, ultimate tensile strength (UTS), and the true fracture stress using the cross-sectional area at the fractured tip. These results were then compared with those obtained in the inert environment, i.e., argon.

RESULTS

In total, forty specimens were tested on the straining machine. The first twelve specimens were annealed together and the specimen number 1, tested in argon, was used as the reference for the specimens 2 to 12. The remaining 28 specimens were annealed under the same conditions but in a different furnace. For some unexplained reason this group came out stronger, and therefore the specimen 14 was tested in argon as a reference for the specimens 13 to 40. Pertinent results from the reference tests are given in Table I.

TABLE I

Mechanical Properties of 2-1/4Cr-1Mo Steel at 25°C
in Argon Obtained at $2.5 \times 10^{-6} \text{ s}^{-1}$ Strain Rate

	UTS ksi	0.2% Offset Y.S. ksi	True Fracture Stress ksi	Total Elongation %	Reduction in Area %
Specimen 1	60.5	37.1	224	37.6	84.2
Specimen 14	67.4	38.7	171	35.5	76.4

Ratios of total elongation, reduction in area, UTS, and the fracture stress at the test condition in the environment, to their respective values in argon are shown in Tables II and III. In Table II results are given for pH 0.5 solutions, whereas in Table III for pHs 4, 7, 10 and 13. Results in the tables are arranged, in any set, in increasing order of the test potential. Results of SEM examinations of the fractured tip and the surface are also summarized in these tables.

Brittle fracture of 2 1/4 Cr-1Mo steel was observed only at cathodic potentials over the entire range of pH from 0.5 to 13, in the sulfide containing solutions. At anodic potentials the fracture in almost all cases was ductile, except when very high corrosion rates led to the dissolution of specimens. The types of failure observed under the different test conditions could be classified into four general kinds:

Brittle failure. Fracture at 45° to major axis, with no necking occurred at potentials which were cathodic to the open circuit potential of the specimen in the test solution. SEM showed cleavage near the surface, gradually changing to more ductile mode at interior of sample. A typical brittle fracture is shown in Fig. 2, the specimen was tested in pH 13 solution with 30 ppm sulfide at -1000 mV_H .

Ductile failure. In the absence of excessive corrosion, the failure at anodic potentials in the sulfide solutions was characterized by extensive necking and dimple structure on the fracture surface. A typical ductile fracture is shown in Fig. 3; the specimen was tested at -700 mV_H in pH 10 solution with 30 ppm of sulfide.

Corrosion failure. It was usually accompanied by extremely high currents, short life, and a smooth or roughened surface. It occurred near the active peak in the polarization curve where the metal is either active or has a protective film broken by the applied stress.

TABLE II

Comparative Mechanical Properties--Elongation Ratio, Reduction in Area Ratio, UTS Ratio and Fracture Stress Ratio of 2-1/4Cr-1Mo Steel in 0.5 pH Solution at Different Potentials and Sulfide Concentrations

Sample No.	T °C	Sulfide ppm	Potential mV _H	Elongation ratio ϵ/ϵ_{Ar}	Reduction in Area ratio $\Delta a/\Delta a_{Ar}$	UTS ratio σ/σ_{Ar}	Fracture Stress ratio σ_f/σ_{fAr}	Failure Mode (1)	Surface (2)
2	25	0	-294	0.85	0.83	1.01	0.68	d	v
3			447	0.04	1.17	0.29	~1.07	c	x
21			500	0.71	1.16	0.68	1.19	c,d	v,w
4			1700	0.98	1.02	1.0	1.01	d	u
12	55	0	-333	0.15	1.14	0.76	0.37	a	u,x
11			-329	0.58	0.99	0.81	0.55	a,d	v,w
16	25	30	-450	0.31	0.62	0.90	0.51	a,b	u
5			-304	0.45	0.35	1.07	0.38	b	u,w
17			-250	0.78	0.85	0.98	0.65	d	v,w
15			-220 (OCP)	0.62	0.49	1.05	0.59	b	u,y
7			500	0.42	1.15	0.81	0.41	a	u,x
18			800	0.92	0.99	1.02	0.67	c,d	u
19			1120	0.85	1.00	1.05	1.03	d	u,y
20			1400	0.89	1.01	1.04	1.12	d	u
6			1700	0.94	0.98	1.08	0.97	d	u
9	55	30	-337	0.56	0.94	0.90	0.64	d	v,w
8			1700	0.52	1.17	0.62	~0.97	a	u,x
10	25	100	-305	0.30	0.23	1.00	0.32	b	u

(1) Failure Mode

- a some crack + extensive corrosion
- b brittle fracture
- c extensive corrosion
- d ductile fracture

(2) Surface

- u light etching
- v severe roughening
- w pitting
- x severe uniform corrosion
- y small cracks
- z large cracks

TABLE III

Comparative Mechanical Properties--Elongation Ratio, Reduction in Area Ratio, UTS Ratio and Fracture Stress Ratio of 2-1/4Cr-1Mo Steel in 4, 7, 10 and 13 pH Solutions at Different Potentials and Sulfide Concentrations.

Sample No.	T °C	Sulfide ppm	Potential mV _H	Elongation ratio ϵ/ϵ_{Ar}	Reduction in Area Ratio $\Delta a/\Delta a_{Ar}$	UTS ratio σ/σ_{Ar}	Fracture Stress Ratio σ_f/σ_{fAr}	Failure Mode (1)	Surface (2)
<u>pH 4</u>									
22	25	30	-330	0.63	1.30	1.05	1.44	a	u,x
23			300			0.34		c	u
24			400	0.64	1.29	0.98	0.78	a	w,x
25			600	0.78	1.04	1.00	1.13	d	w
13	25	100	-380	0.42	0.16	1.22	0.35	b	y,z
<u>pH 7</u>									
28	25	30	-800	0.63	0.46	1.04	0.38	b	y,z
27			-600	0.80	0.90	1.03	0.77	d	y,z
26			-500	0.88	0.99	0.97	1.09	d	u
29			400	0.72	1.25	1.00	0.82	c,a	w,x
30			400	0.32	1.25	0.75	1.02	c,a	w,x
<u>pH 10</u>									
36	25	0	-850	0.72	0.70	0.99	0.65	d,b	y,z
35			380	0.46	1.29	0.88	1.13	c,a	w,x
33	25	30	-850	0.68	0.43	1.03	0.46	b	y,z
32			-700	0.92	0.94	0.97	0.79	d	y,z
31			-450	0.70	1.03	0.97	1.03	d	v
34			380	0.71	1.27	0.95	0.81	c,a	u,x
<u>pH 13</u>									
40	25	30	-1000	0.62	0.49	1.02	0.55	b	y,z
39			-850	0.84	0.94	0.95	0.75	d	y,z
38			-750	0.68	0.96	0.97	0.98	d	y
37			-238	0.81	0.99	1.02	0.98	d	y

(1) Failure Mode

- a some crack + extensive corrosion
- b brittle fracture
- c extensive corrosion
- d ductile fracture

(2) Surface

- u light etching
- v severe roughening
- w pitting
- x severe uniform corrosion
- y small cracks
- z large cracks

Figure 2. A typical brittle fracture of 2-1/4Cr-1Mo steel. The specimen was tested at -1000 mV_H in pH 13 solution with 30 ppm sulfide.

Figure 3. A typical ductile fracture of 2-1/4Cr-1Mo steel. The specimen was tested at -700 mV_H in pH10 solution with 30 ppm sulfide.

Ambiguous. The failure mode in the potential region of imperfect passivity was of mixed nature with signs of both corrosion and brittle fracture. During straining the increasing load suddenly starts dropping slowly and nearly linear with time; the current increases greatly--probably due to the active dissolution, until the crack is eaten out or the metal repassivates. The test then continues with the specimen behaving in a ductile manner until the cracking is repeated or ductile fracture occurs. Fractured specimens showed a sharp ring cut around the tip, often at 45° to the major axis. The surface showed also roughening due to general corrosion. A typical fracture is shown in Figure 4; the specimen was tested in pH 4 solution with 30 ppm sulfide at -330 mV_H . The failure process could best be described as stress-assisted corrosion.

Based on the mechanical properties alone, it is difficult to differentiate between a ductile and brittle fracture in many cases. In general, the fracture was ductile if the elongation ratio was >0.56 but brittle <0.68 . Similarly, if the reduction in area is <0.5 brittle fracture could be expected.

DISCUSSION

Fracture appearance of 2-1/4Cr-1Mo steel as a function of pH and potential is summarized in Figure 5. As could be seen in the figure all the brittle fractures occurred at potentials which are quite negative to the hydrogen evolution line. Further, the potential for the brittle fracture decreased with an increase in pH. The brittle fracture is most likely due to the hydrogen embrittlement of the steel. The role played by the sulfide was merely to promote the entry of hydrogen into the metal. This role of sulfide is well known (1).

Figure 4. A typical stress assisted corrosion fracture of 2-1/4Cr-1Mo steel. The specimen was tested at -330 mV_H in pH 4 solution with 30 ppm sulfide.

Figure 5. Fracture appearance of slow strain rate test specimens as a function of potential and pH.

CONCLUSIONS

The 2-1/4Cr-1Mo steel is susceptible to cracking in sulfide environment only at potentials in the cathodic region. The cracking is most probably due to hydrogen embrittlement. At anodic potentials the failures in straining tests were due to either the general corrosion or mechanical ductile fracture.

REFERENCE

1. R.D. McCright, in Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys, Eds. R.W. Staehle, J. Hochmann, R.D. McCright and J.E. Slater, NACE-V, Houston, Texas (1978).

TASK 2

Fundamental Electrochemical and Corrosion Studies of Pure Iron and Selected Alloys in Aqueous Sulfide Environment

R. Koehler, A.K. Agrawal, and R.W. Staehle

INTRODUCTION

The objective of this task is to study the corrosion kinetics and the composition of films formed on pure iron, and its selected alloys in aqueous sulfide environments as a function of pH and potential.

RESULTS

The apparatus, electrochemical cell and the electronic instruments have been assembled to pursue this task. A literature search has also been done on the sulfide corrosion problem.

At the time of reporting only a few trial runs with pure iron in H_2S saturated water have been made. No significant data is available for reporting in this period.

TASK 3Fundamental Measurements of Stress Corrosion Cracking
Parameters Including Inhibitors in the Caustic Environment

U. Kim, A.K. Agrawal, and R.W. Staehle

INTRODUCTION

In the previous report (1), see also reference (2), it was shown that the stress corrosion cracking behavior of Fe-Cr-Ni alloys in the caustic environment can be readily evaluated as a function of potential by the use of straining electrode technique. The straining electrode technique was used to measure crack propagation rates (CPRs) of Type 304, Incoloy 800, and Inconel 600 alloys in boiling concentrated caustic solutions. From a comparison of CPRs of the 3 alloys at different potentials, the role of the constituent elements in the CPR of the Fe-Cr-Ni alloys was speculated. The CPRs of the alloys are shown in Figure 1, whereas the role of constituent elements is pointed out in Table I.

TABLE I

<u>Potential Region</u>	<u>CPR Trend</u>	<u>Controlling Element</u>
Active	I-600 > AISI 304 > I-800 15 < 18 < 20	Cr%
Passive	AISI 304 > In-800 > In-600 10 < 30 < 75	Ni%
Transpassive	In-600 > AISI 304 > In-800 15 < 18 < 20	Cr%
Pseudo-Passive	AISI 304 > In-800 > In-600 10 < 30 < 75	Ni%

Figure 1. The CPR and i_b/i_s ratio as a function of potential for the alloys AISI 304 in 20N NaOH and Inconel 600 and Incoloy 800 in 17.5 NaOH solution.

It is shown in Table I that Ni is the rate controlling element in the CPR of the alloys in their passive and the pseudo-passive region. But near the $-0.7 V_H$, near the active region of the alloys, Ni may be detrimental. The objective of the present investigation was to study the commercially pure Ni with the straining electrode technique in order to relate the above observation with the CPR in Ni at different potentials, and to understand the mechanism of cracking. A second objective of the present task was to use the straining electrode technique to compare the CPRs in the annealed Type 304 in concentrated NaOH solution with that in the annealed and sensitized Type 304; the later is known to be more susceptible to cracking in the caustic solution, see Appendix A.

EXPERIMENTAL

Experimental details and the calculation procedure for the CPR are described in (1) and (2). Specimens used in the present study, however, were different from the previous study. Instead of wire specimens, waisted tensile bar specimens of 6.25 mm diameter and 23 cm length were used. The gage section in the bar was 12.5 mm long and 2.5 mm in diameter. The change was necessary in order to avoid leaking problem at the bottom of the Teflon cell.

Nickel specimens were machined from commercially as-drawn pure Ni-200 alloy. The analysis of the alloy was: Ni 99.65%, Mn 0.25%, Fe 0.01%, Cu 0.01%, Si 0.02% and S 0.002%. Specimens were used in the machined condition after cleaning, without any heat treatment.

Type 304 stainless steel used for specimens was actually Type 304L. This was done because of a large number of Type 304L tensile specimens were available in the laboratory, which were left over from the other projects at the Ohio State University. Type 304L specimens were given two different heat treatments; first, all the specimens were annealed at 1100°C for 2 hours in vacuum and water quenched, then some of the quench annealed specimens were sensitized at 650°C for 10 hours and furnace cooled. A metallographic examination of the specimens showed large grains, due to the annealing heat treatment. However, the sensitization heat treatment failed to produce carbide precipitation at the grain boundaries. This was due to the low carbon in the steel and also due to the relatively long exposure time at 650°C, which allowed healing.

The strain rate used in all the tests was 55%/min. The current density, i_b , on the bared surface was measured at ~13% elongation, for the CPR calculation. The solution used in the tests was 17.5N NaOH at its boiling point ~138°C. Chromate addition to the solution was made in some instances, the $\text{CrO}_4^{=}$ concentration was 0.005M.

RESULTS AND DISCUSSION

Nickel-200

Results of the straining experiments with Ni-200 in 17.5N NaOH at 138°C are shown in Figure 2. The i_b values are approximately 2 orders of magnitude higher than the corresponding i_s values, over the entire potential range from $-0.75V_H$ to $0.2V_H$. The highest i_b value of nickel is between -0.7 and $-0.6V_H$, and the lowest near the corrosion potential.

Figure 2. The current density on the filmed metal, i_s , and the calculated current density on the bare metal, i_b , at different potentials for Nickel-200 in 17.5N NaOH solution at 138°C.

(The initial corrosion potential of cathodically reduced Ni is about $-0.9V_H$, but the potential gradually drifts to a quasi-steady state value of $-0.76V_H$).

The calculated values of CPR and i_b/i_s ratios as a function of potential are shown in Figure 3. The CPR is lowest, $\sim 2 \times 10^{-10}$ m/s, just near the corrosion potential of Ni-200 in the solution, and the highest, $\sim 10^{-8}$ m/s, in the active peak region between -0.6 and $-0.7 V_H$. The CPR is nearly uniform, $\sim 10^{-9}$ m/s, at potentials above $-0.6V_H$, i.e., in the passive region. A high nickel alloy, e.g., Inconel-600, is therefore likely to have CPR values of the order of 10^{-8} m/s in the potential range -0.7 to $-0.6V_H$, but low values in the passive range. The CPR values for Inconel 600 in Figure 1 show this trend up to the passive potential of $-0.2V_H$. However, above this potential, i.e., in the transpassive and the pseudo-passive regions of the alloy, the rates are higher than the corresponding rates for Ni-200. At potentials above $-0.2V_H$, due to the high instability of chromium the influence of nickel is lessened. But the influence of Ni is still apparent in Figure 1 when the CPRs of the low Ni alloys are considered.

In Figure 3, the i_b/i_s ratios for Ni-200 are consistently high, $>10^2$, at all the potentials. The highest value being $\sim 10^3$ at $-0.7V_H$. The high values suggest that the corrosion attack or cracking in Ni-200 is likely to be extremely localized. The high i_b/i_s ratios for nickel is appropriately reflected in high values of the order of 10^2 for Inconel 600 in Figure 1. In the previous report it was pointed out that the attack observed on Inconel-600 are indeed intensely localized in comparison to the other alloys. The present results confirm that the localized attack is primarily due to the high nickel in Inconel-600.

Figure 3. Calculated crack propagation rate and current ratio i_b/i_s at different potentials for Ni-200 in 17.5N NaOH at 138°C.

Type 304L

Results, the quasi-steady state current density (i_s) and the corresponding current density at the bared surface (i_b), of the straining experiments with Type 304L as a function of potential are shown in Figures 4 to 6. Results in Figure 4 are for the quench annealed material, and in Figure 5 for the quench annealed and sensitized material tested in 17.5 NaOH at 138°C. Whereas results for the quench annealed material tested in the presence of $0.005M CrO_4^{=}$ in 17.5N NaOH at 138°C are shown in Figure 6.

There is a marked difference between the i_s vs. potential curves in Figure 4 and 5. The anodic reactivity of the sensitized metal is slightly higher than that of the annealed material, at all the potentials, except in the passive region between -0.4 and $-0.6 V_H$. The current in the passive region for the sensitized material is cathodic, while it is anodic for the annealed material. The difference suggests that the sensitization heat treatment did affect the reactivity of the alloy surface, even though the metallographic examination failed to show appreciable change in the microstructure. The cathodic loop in Figure 5 suggests an extremely good passive film on the metal surface and the presence of a reducible specie either on the surface or in the solution. The i_s values for annealed material in Figure 6, the chromate containing solution is also cathodic, but below the open circuit potentials $-0.56V_H$ due to the reduction of $CrO_4^{=}$ ions. On the other hand, i_b values for all the three systems are anodic at all the potentials.

The CPRs and i_b/i_s ratios for the above 3 systems are shown together in Figure 7 as a function of potential. The CPR for the three cases show identical values at high anodic potentials above $-0.4V_H$. The differences in

Figure 4. The current density on the filmed metal, i_s , and the calculated current density on the bare metal, i_b , at different potentials for annealed Type 304L in 17.5N NaOH solution at 138°C.

Figure 5. The current density on the filmed metal, i_s , and the calculated current density on the bare metal, i_b , at different potentials for annealed and sensitized Type 304L in 17.5N NaOH solution at 138°C.

Figure 6. The current density on the filmed metal, i_s , and the calculated current density on the bare metal, i_b , at different potentials for annealed Type 304L in 17.5N NaOH + 0.005N CrO₄⁼ solution at 138°C.

Figure 7. The CPR and i_b/i_s ratio as a function of potential for the annealed and the sensitized Type 304L in 17.5N NaOH solution at 138°C. Δ solution contained 0.005M $\text{CrO}_4^{=}$.

values between $-10.$ and $-0.4V_V$ are also nominal. The CPRs in the $CrO_4^{=}$ containing solution are lowest of the three, below $-0.4V_H$. The chromate ion was found to be a good inhibitor of stress corrosion cracking in boiling 20N caustic solution for Type 304 under static load tests (1). The present results indicate that under conditions where the surface film might be ruptured periodically such as under high cyclic stress the chromate ions may not provide adequate inhibition. In fact, this has been demonstrated for Type 304 at the Ohio State University.

A clear distinction between the CPRs of the annealed and the sensitized material could not be made in the present investigation because Type 304L could not be sensitized properly.

The i_b/i_s ratios for the three cases are also almost identical at all the potentials, except for the sensitized material between -0.5 and $-0.7V_H$. If the passive current in this potential region is assumed to be $1\mu A/cm^2$, a very high, $\sim 10^3$, ratio would be obtained for the i_b/i_s . This would indicate a very localized attack on the sensitized material in comparison to that on the annealed material. The stress corrosion cracking in sensitized material is usually intergranular, see Appendix A, and this supports the high values of i_b/i_s ratio.

CONCLUSIONS

The following conclusions can be made from the straining electrode results.

The CPR in Nickel-200 in 17.5N NaOH at $138^\circ C$ is high on the order of $10^{-8} m/s$ in the potential range -0.6 to $-0.8V_H$. A high nickel alloy, e.g., Inconel-600 in the above potential region is likely to have a high CPR

due to the influence of Ni. At potentials outside the above range the CPRs are relatively low, $\sim 10^{-9}$ m/s, and therefore nickel in the Fe-Cr-Ni has a beneficial effect.

The CPRs in Type 304L in the 17.5N NaOH at 138°C are not significantly different when 0.005M $\text{CrO}_4^{=}$ is added to the solution. The $\text{CrO}_4^{=}$ ions do not offer rapid inhibition under transient conditions. Therefore, $\text{CrO}_4^{=}$ ions which have been shown to offer excellent inhibition of stress corrosion cracking under constant load conditions, may not be protective in fatigue conditions where the film is broken periodically.

REFERENCES

1. R.W. Staehle and A.K. Agrawal, OSU Report No. C00-2421-04 (1978).
2. Y.S. Park, J.R. Galvele, A.K. Agrawal and R.W. Staehle, Corrosion, in press, (expected February 1979).
3. A. Boateng in "Corrosion and Corrosion Cracking of Materials for Water Cooled Reactors," FCC 7702, OSU (1977).

TASK 4Fundamental Electrochemical and Corrosion Studies of
Pure Metals Fe, Cr, and Ni in the Caustic Environment

U. Kim, A.K. Agrawal, and R.W. Staehle

INTRODUCTION

The objective of the present study is to investigate the electrochemical and corrosion behavior of pure metals Fe, Ni and Cr in the caustic environment. Potentiodynamic polarization curves give only limited information regarding the active-passive behavior of the metal; the curves cannot be relied upon for describing the long term corrosion behavior in the test environment. For example, pure nickel at $-0.6V_H$ in 17.5N NaOH solution shows large active peak, with a current density of $4 \times 10^{-3} A/cm^2$, indicating a rapid corrosion at this potential (1). However, when a nickel specimen is potentiostated at $\sim -0.6V_H$ for a long period of time no appreciable corrosion is detected. Therefore in the present work, long term corrosion behavior of metals has been investigated using the current decay measurements. The slope of decay curves can be used in determining the film formation processes and rate laws.

It was shown, in the previous report (1), that for Ni in caustic solution an induction time is necessary before the passivation occurs. It was also shown that the induction time is the time required to saturate the hydrodynamic boundary layer around the electrode with the dissolved nickel ions, probably $HNiO_2^-$. At this time a film precipitates on the surface from the saturated solution. The film growth thereafter proceeds in a logarithmic form with a slope of $d \log i / d \log t = -1$, characteristic slope for a place-exchange process of film growth.

In the present task work is extended to pure Fe and Cr in the caustic solution. In order to understand the processes occurring in the first few milliseconds after applying the potential, transient chronoamperometric response has also been measured with an oscilloscope.

EXPERIMENTAL

The experimental technique and procedure with Fe and Cr were essentially the same that were used with Ni, and which are described in (1). A mechanically polished specimen was first cathodically treated at -1250 mV (Hg/HgO) in deaerated 17.5N NaOH to remove the air formed film, and to get a clean surface. The potential was then jumped to a desired value. The current transient was followed on a Tectronix Oscilloscope, whereas the current decay was followed on a strip chart recorder.

RESULTS AND DISCUSSION

Transient Chronoamperometric Response

Current responses in the first 10 or 20 milliseconds, after stepping the potential, are shown in Figures 1 to 3 for Fe, Cr, and Ni in 17.5 NaOH solution at 130°C. In each figure responses are shown for several stepping potentials. It is seen in the figures that the anodic current reached a peak value within 2 milliseconds after applying the potential. The peak current for any metal is strongly dependent upon the applied potential, the peak current increased with the potential. After reaching the peak the current decayed within 3 to 8 milliseconds, depending upon the potential and the metal, to a short time steady value.

Total charge passed up to the peak time was calculated for each case. This peak charge, Q_p , is shown as a function of potential in Figure 4 for Fe, Cr, and Ni. A practically straight line relationship is seen between Q_p and V . This suggests that the main process occurring on the electrode surface in the first 2 milliseconds is the charging of the double layer. Thus, the double layer capacitance, C_{dl} , can be easily calculated from the slope $\Delta Q/\Delta V$, while assuming that the faradaic contribution in this time period is negligible. Since the peak time represents only half of the charging time, the double layer capacitance can be approximated by $C_{dl} \approx 2\Delta Q_p/\Delta V$. The value thus obtained for Fe, Cr and Ni in 17.5N NaOH at 130°C is approximately 15,000 $\mu\text{f}/\text{cm}^2$.

Current Decay Curves

Current decay curves for Ni have been reported in the previous report. The curves for Cr and Fe in 17.5N NaOH solution at 130°C are shown in Figures 5 to 8. The curves in Figure 5 are for Cr in the potential region -900 to -700 mV (Hg/HgO) which is below the active peak region, whereas those in Figure 6 are for the passive and transpassive regions. Similarly, the curves for Fe in Figure 7 are for the lower potential regions, and that in Figure 8 for the upper passive region.

An induction time for passivation of Cr is observed, similar to that of Ni, in Figures 5 and 6 at all potentials except the transpassive potentials -200 and -100mV (Hg/HgO). The induction time is potential dependent, but in all the cases it is less than 0.5 seconds. The slope of current decay curves is -1.0 at potentials from -900 to -700 mV (Hg/HgO), but slightly higher -0.85 at potentials up to -300 mV (Hg/HgO). At the transpassive potentials the slope is substantially higher due to Cr dissolution as $\text{CrO}_4^{=}$. The slope

-0.85 in the passive region of Cr could be considered as ~ -1.0 , similar to that at lower potentials. This would suggest that a place-exchange mechanism of Cr at all the potentials below the transpassive region. The passive film on the metal is probably hydrated $\text{Cr}(\text{OH})_3$.

The current decay curves for Fe are totally different from that for Ni and Cr. High currents are observed from the start ($< 10^{-2}$ minutes) to almost 10^3 minutes. There is no passivation observed in this time period at any potential from -1000 to -200 mV (Hg/HgO). If iron oxides Fe_3O_4 , $\text{Fe}(\text{OH})_2$, Fe_2O_3 , or $\text{Fe}(\text{OH})_3$ are formed at different potential on the surface, these oxides are not protective.

A comparison of current densities for the three metals Fe, Cr, and Ni after 10 minutes polarization at different potentials are shown in Figure 9. It is clearly seen that Cr has the lowest current density at all the potentials below the transpassive region of Cr, i.e., -200 mV (Hg/HgO). This suggests that the Cr has the best corrosion resistance in the caustic solution. Whereas the Ni is the next best in corrosion resistance, and the Fe is poorest. In very oxidizing conditions, however, Cr will be unstable and dissolve as $\text{CrO}_4^{=}$ ions.

CONCLUSIONS

In concentrated caustic solution a protective passive film forms on the metals Cr and Ni, over a wide range of potentials. The film formation occurs after an induction time which is potential dependent. The film growth thereafter is by place-exchange mechanism. On the other hand, the film formed on Fe is not protective at any potential.

REFERENCE

1. R.W. Staehle and A.K. Agrawal, OSU Report C00-2421-04 (1978).

Figure 1. Current versus time data at controlled potentials for Fe in deaerated 17.5N NaOH at 130°C. One vertical division is 0.2A and one horizontal division is 2 milisecond. Surface area is 0.548 cm² and cathodic pretreatment is at -1.1V_H for 4 minutes.
 1) -0.4V_H 2) -0.5V_H 3) -0.6V_H 4) -0.7V_H 5) -0.8V_H 6) -0.9V_H

Figure 2. Current versus time at controlled potentials for Cr in deaerated 17.5N NaOH at 130°C. One vertical division is 0.2A and horizontal division is 1 milisecond. Surface area is 0.480 cm² and cathodic pretreatment is at -1.25V_H for 4 minutes.
1) -0.2V_H 2) -0.4V_H 3) -0.6V_H 4) -0.8V_H

Figure 3. Current versus time at controlled potentials for Ni in deaerated 17.5N NaOH at 130°C. One vertical division is 0.2A, one horizontal division is 1 milisecond. Surface area is 0.404 cm² and cathodic pretreatment at -1.25V_H for 4 minutes.

1) -0.2V_H 2) -0.4V_H 3) -0.6V_H 4) -0.8V_H

Figure 4. Total coulombic charge at the peak of the current transient as a function of potential for Fe, Cr, and Ni in 17.5N NaOH at 130°C.

Figure 5. Current density vs. time at different potentials for Cr in 17.5N NaOH at 130°C.

Figure 6. Current density vs. time at different potentials in the passive and the transpassive regions for Cr in 17.5N NaOH at 130°C.

Figure 7. Current density vs. time at different potentials for Fe in 17.5N NaOH at 103°C.

Figure 8. Current density vs. time at different potentials in the passive region for Fe in 17.5N NaOH.

Figure 9. Current density vs. potential for Fe, Cr, and Ni in 17.5N NaOH at 130°C after 10 minutes of polarization at each potential.

THE STRESS CORROSION CRACKING BEHAVIOR OF
TYPE 304 STAINLESS STEEL IN BOILING
50% NaOH SOLUTION

D.V. Subrahmanyam*, A.K. Agrawal**, R.W. Staehle**

ABSTRACT

The stress corrosion cracking susceptibility of Type 304 stainless steel has been studied in 50% NaOH solution at the open circuit potential and at controlled potentials. The alloy was tested in two heat treated conditions--annealed for 2 h at 1200°C, and sensitized for 10 h at 538 °C. The sensitized alloy failed due to intergranular SCC at all potentials below the transpassive potential, and above by pitting and general corrosion. The annealed alloy suffered transgranular SCC at the open circuit potential and at cathodic potentials. In the pseudo-passive region, intergranular SCC occurred. Type 304 suffers some general corrosion at all the potentials, irrespective of its heat treatment.

The estimated crack propagation rate at the open circuit potential for the annealed alloy in boiling 50% NaOH solution was of the order of 10^{-10} m/s. The threshold stress for the transgranular SCC at this potential is <20% of the yield stress of the alloy.

* Present address: Ontario Hydro, Toronto, Ontario, Canada.

** Department of Metallurgical Engineering, Ohio State University
Columbus, Ohio 43210, USA.

INTRODUCTION

The performance of Fe-Cr-Ni alloys in the caustic environment at elevated temperatures is of interest to the nuclear and also to the fossil fuel power industry, as well as to the manufacturers and the users of caustic. Several recent papers (1 to 8) have described the various aspects of caustic stress corrosion cracking (SCC) in the commercial Fe-Cr-Ni alloys. Conflicting claims have been made sometimes with respect to the effects of caustic concentration, temperature, the presence and the absence of dissolved oxygen in the solution, sensitization, and the role of constituent elements in the alloy on the SCC.

The objective of the present study was to systematically study the effect of applied potential on the SCC behavior of Type 304 stainless steel in 50% NaOH solution at its boiling point. This NaOH concentration is a nearly saturated solution at room temperature and offers a high test temperature, $\sim 148^{\circ}\text{C}$, without recourse to a pressurized system. Other aspects of SCC will be dealt with in a future paper.

EXPERIMENTAL

A commercial grade Type 304 stainless steel wire with 18.3% Cr and 11.8% Ni was used in the tests. Diameter of the wire was 0.38 mm. The as-received wire was cut into ~ 30 cm lengths for specimens. These, after degreasing with acetone, were encapsulated in evacuated quartz tubes for heat treatment. The specimens were heat treated in two different ways, one set was annealed at 1200°C for 2 h and water quenched, while the other set was sensitized at 538°C for 10 h and furnace cooled.

All the tests were made in $\sim 50\%$ NaOH solution which was prepared from a carbonate free NaOH and double distilled water. The test temperature was the boiling point of the solution, 148°C , unless mentioned otherwise.

A number of Teflon cells were used for the constant load SCC experiments.

One such cell assembled with a specimen and the load is shown in Fig. 1. The cell is heated from the outside, and it is provided with a condenser to prevent the loss of water due to evaporation during a test. Time to failure (t_f) of the specimen is automatically recorded on a multi-channel Esterline Angus event recorder. Unless mentioned otherwise the specimens were loaded to 100% of their yield stress (y.s.) with fixed load. A test was terminated if the specimen did not fail in 15 days. All the specimens after the SCC tests were examined metallographically.

The SCC tests were done at the open circuit potential (OCP) and also at controlled potentials which covered a range from the HER almost to OER. The reference electrode used was a saturated calomel electrode, it was kept outside the cell at room temperature. A Teflon tube 6.2 mm o.d. and 3 mm i.d. with a nylon wick inside wetted with the test solution formed the Luggin probe. The other end of the probe was outside the cell, immersed in a room temperature NaOH solution, which in turn was connected to the reference electrode via a KCl bridge. All the measured values of potential were converted to the standard hydrogen scale for reporting by adding 242 mV. A Pt wire placed inside the cell served as a counter electrode in the controlled potential tests. In these cases the current was recorded until the end of a test.

Polarization curves were made on unstressed specimens. The polarization was done at a stepping rate of 20 mV/5 m starting from the cathodic potential and stepped in the noble direction. The current was recorded for reporting at the end of a 5 minute interval.

RESULTS

Polarization Curves

The anodic and the cathodic polarization curves for the annealed Type 304 and the sensitized Type 304 are shown in Fig. 2. The anodic curves for both the heat treatments show an active region, a passive region, a transpassive

Figure 1 - Teflon test cell.

Figure 2 - Time to failure vs. potential; and the polarization curves for Type 304 in 50% NaOH at 148°C.

Figure 3 - Time to failure at 148°C vs. load; and time to failure at 100% y.s. vs. temperature for Type 304 in 50% NaOH.

region,* and a pseudo-passive region--above -200 mV_H . There are multiple peaks in the active region, and these are more pronounced for the sensitized alloy in comparison to the annealed alloy. The lower active peak is due to Fe, and the top peak is due to Ni, see reference (7). The transpassive region, between -400 and -200 mV_H , is mainly due to the oxidation of Cr or Cr_2O_3 to $\text{CrO}_4^{=}$. The pseudo-passivation above -200 mV_H results mainly from a diffusion limited reaction and the deposition of corrosion products on the specimen surface. In this potential region, the current for the annealed alloy is slightly higher in comparison to the sensitized alloy; the opposite is true at lower potentials. The cathodic behavior is indential for both the cases.

Time to Failure at OCP

The effect of applied stress, and that of temperature on the t_f of annealed Type 304 at the open circuit potentials are shown in Fig. 3. The t_f above 30% of y.s. decreased logarithmically with increasing stress in the boiling 148°C solution. At a stress lower than 30% of y.s. the t_f was considerably high, $\sim 540 \text{ h}$ at 20% of y.s. This is probably due to the stress approaching the threshold value of SCC. The crack propagation rate in the alloy estimated from the t_f vs. load data is $\sim 3 \times 10^{-10} \text{ m/s}$. The rate was calculated on the assumption that a specimen fractures under a constant load when the stress exceeds the ultimate tensile stress of the alloy due to the reduced cross-section from crack penetration. The t_f at 100% of y.s. decreased with the increasing temperature, as would be expected. The decrease was significant when the temperature jumped from 142 to 148°C , but it was gradual between 128 to 142°C .

Time to Failure Vs. Potential, and Crack Morphology

Time to failure results at different potentials are shown in Fig. 2 against polarization curves for both the annealed and the sensitized Type 304. Crack morphologies of specimens tested at different potentials are shown in Fig. 4 for the two heat treatments.

Figure 4 - Crack morphology at different potentials for the quench annealed and the sensitized Type 304 in 50% NaOH at 148°C. Potential in mV_H and the failure time in hour are shown on each photomicrograph.

The sensitized alloy failed in short time, between 15 and 35 h, at all potentials below the passive potential of -454 mV_H , but the t_f was above 100 h at -454 mV_H . The t_f was short again, $<45 \text{ h}$, in the transpassive region between -350 and -200 mV_H . In the pseudo-passive region the t_f was above 100 h and it improved with the anodic potential $>-200 \text{ mV}_H$. A specimen tested at $+245 \text{ mV}_H$ failed in 350 h. The crack morphology at all the potentials $<-200 \text{ mV}_H$ was predominantly intergranular but was accompanied with some general corrosion, see Fig. 4. The specimens failed primarily due to IGSCC. Above -200 mV_H the mode of attack was overlapping pits resembling general corrosion, which changed to uniform corrosion at higher potentials.

The annealed alloy, similar to the sensitized alloy, also failed in a short time, $<50 \text{ h}$, at cathodic potentials below the OCP down to -1105 mV_H . However, unlike the IGSCC observed in the sensitized alloy, the annealed alloy suffered blunted transgranular stress corrosion cracking and some general corrosion, see Fig. 4. At a lower cathodic potential of -1154 mV_H the t_f increased to 115 h; the attack was as described above but less severe. Near the OCP, at -955 mV_H , the specimen failed in 103 h due to TGSCC. At potentials in the active region the annealed alloy failed in $\sim 100 \text{ h}$ and the principal mode of attack was uneven general corrosion.

The annealed alloy showed excellent resistance to cracking in the passive potential region between -655 and -355 mV_H . Specimens did not fail in 360 h of testing. In the lower passive region ca. -655 mV_H there was practically no attack. But as the potential approached the transpassive region, specimens showed incipient cracks, e.g., at -455 and -355 mV_H , see Fig. 4. At potentials above -355 mV_H , the t_f decreased first gradually then sharply with the potential, as opposed to the increase in t_f for the sensitized alloy in the same region. The annealed specimens failed primarily due to pitting and IGSCC up to about $+45 \text{ mV}_H$. Above $+45 \text{ mV}_H$ the specimens

failed rapidly in less than 20 h due to IGSCC.

Current Vs. Time

The current response of stressed specimens at different potentials is given in Fig. 5 for the sensitized alloy, and in Fig. 6 for the annealed alloy. For the sensitized alloy the current at potentials -1155 and -1054 mV_H was cathodic of the order of 6×10^4 μ A for the first ~ 3 h and then decreased sharply by 2-3 orders of magnitude until fracture occurred. The drop is probably due to the increased anodic activity at the crack tips resulting from the IGSCC. In the active potential region at -955 and -855 mV_H the anodic current was $\sim 10^2$ μ A in the beginning; it showed a 5 fold jump after about 4 h leading to fracture. In the passive potential region the current in the initial period was comparatively low $< 10^2$ μ A; a sudden increase was observed for different potentials at different times--after 1.5 h at -655 mV_H, and after 25 h at -554 and -455 mV_H. The current response at the transpassive potential -255 mV_H was opposite to that at lower potentials. The current increased from 2.2×10^2 μ A to 2.5×10^3 μ A in the first 4 h and then decreased until the fracture of the specimen due to thinning and IGSCC. No current

Figure 5 - Current vs. time at different potentials for the sensitized Type 304 at 100% y.s. in 50% NaOH at 148°C.

Figure 6 - Current vs. time at different potentials for the quench annealed Type 304 at 100% y.s. in 50% NaOH at 148°C.

transitions were observed in the pseudo-passive region, e.g., at -55 mV_H the current decreased monotonously from a high $1.7 \times 10^3 \text{ } \mu\text{A}$ value to $10^2 \text{ } \mu\text{A}$ at fracture, reflecting general corrosion of the specimen.

The current for the annealed alloy was cathodic at potentials -955 mV_H and below; unlike the sensitized alloy, a transition in the current was not seen at potentials -1154 and -1054 mV_H , and the current response was relatively uneventful. Near the OCP at -955 mV_H the cathodic current decreased uniformly from 1.6×10^3 to $2.3 \times 10^2 \text{ } \mu\text{A}$ in the first 7 h and then rose steadily until fracture at $6 \times 10^3 \text{ } \mu\text{A}$. The initial drop in the current could be attributed to the increased anodic activity on the specimen due to TGSCC, but the subsequent rise suggests either a drop in the anodic activity with time or an increase in the ratio of the cathodic to anodic area with the progress of cracking. In the active region at -855 mV_H the anodic current increased for about 3 h from initial $1.2 \times 10^2 \text{ } \mu\text{A}$ to $7.2 \times 10^2 \text{ } \mu\text{A}$ and then gradually dropped and increased again at ~ 17 h until failure. The oscillation in the current is probably associated with the surface roughening and thinning of the specimen due to general corrosion. At -755 mV_H the anodic current increased from $12 \text{ } \mu\text{A}$ to $3.5 \times 10^2 \text{ } \mu\text{A}$ in ~ 17 h and decreased thereafter to a negligible value, but turned cathodic near the end. The initial rise may have been due to the surface roughening from the uneven general corrosion, but the significance of the cathodic current is not clear.

In the passive region between -655 and -355 mV_H the anodic current was low $< 60 \text{ } \mu\text{A}$ throughout the test, it decreased further to negligible value after about 100 h. It appears that in the passive region a film grows for about 100 h at which time it becomes very protective, resulting in the drop of current. This protective film must have been responsible for no failure of the specimens. The current response at the transpassive potential -255 mV_H was similar to that in the passive region up to about 100 h,

thereafter the response differed; the current stayed constant at $\sim 55 \mu\text{A}$ indicating that this film was not fully protective. The specimen failed in a long time due to pitting. In the pseudo-passive region the high initial current, $\sim 10^3 \mu\text{A}$ or greater, decreased monotonously until fracture occurred due to pitting and IGSCC. The high current masked the damaging events from being reflected as transients.

DISCUSSION

The present results show a strong influence of potential on the SCC behavior of Type 304 in boiling 50% NaOH solution. The time to failure as well as the crack morphology of both the annealed and the sensitized alloy were affected by the potential. The effect of potential was more varied for the annealed than for the sensitized alloy. The various effects at different potentials can be broadly grouped in five different regions associated with the polarization curve of Type 304.

For the sensitized alloy the t_f was nearly uniform and short up to the transpassive region and the failures were primarily due to IGSCC. The t_f was longer in the pseudo-passive region and the mode of attack was general corrosion. Whereas for the annealed alloy the t_f was short in the cathodic region where TGSCC occurred. The t_f somewhat improved in the active region where the failures resulted from the general corrosion. No failures and practically little attack corresponded to the passive region. Annealed specimens in the transpassive region failed in a relatively longer time due to pitting. And finally, in the pseudo-passive region a short t_f was caused by IGSCC.

The above findings for the annealed alloy have been recently confirmed by Park, et al. (8). One slight difference they have noticed is in the pseudo-passive region; the IGSCC after some penetration switched to TGSCC in their case. Park et al. used a thicker specimen than used in the present study, and their test solution was 20N NaOH + 0.005M Na_2CrO_4 .

at 150°C. Further, they found that near the second active peak, a potential not investigated in this study, the t_f was extremely short <8 h, and the failure was due to stress assisted general corrosion. And at potentials near -1200 mV_H, the immunity region of metals on the Pourbaix diagram, there was practically no attack or cracking.

The current response at different potentials qualitatively reflects the nature of the cracking process for most cases. The sudden rise in the anodic activity after a certain time interval at potentials below the transpassive region, especially for the sensitized alloy is probably associated with the initiation of IGSCC. The time interval before the jump is thus the induction time for IGSCC. This time, in a general way, improved from ~2 to 25 h with increasing potential. In the case of pitting and general corrosion at high potentials, no jump in the anodic activity was observed; on the contrary the anodic current dropped after a while due to the thinning of the specimen and the buildup of corrosion products on the surface.

For the annealed alloy the absence of a sudden rise in the anodic activity in the region of TGSCC suggests probably an absence of induction time for this heat treatment. Similarly at the high potentials corresponding to the IGSCC region no sudden rise was observed.

Due to the limitation of space in this paper, the mechanistic aspects of cracking have not been discussed. The cracking, both the TGSCC and the IGSCC are believed to be due to the anodic dissolution at the crack tip.

CONCLUSIONS

Type 304 stainless steel is susceptible to SCC in 50% NaOH at 148°C in only certain potential regions. These regions change with the heat treatment of the alloy.

The annealed alloy is susceptible to TGSCC near its OCP and down to

200 mV below. It is susceptible to IGSCC, which may switch after some penetration to TGSCC, in the pseudo-passive region. The alloy is least susceptible to SCC in its passive region.

The sensitized alloy is susceptible to IGSCC over a broad range of potentials from about 200 mV below the OCP to the transpassive range. In the pseudo-passive region pitting and general corrosion occur on the sensitized alloy.

Some general corrosion occurs on Type 304 in 50% NaOH at 148°C at all the potentials, irrespective of the heat treatment.

ACKNOWLEDGEMENT

This work was supported by a grant from the United States Department of Energy.

REFERENCES

1. I.L.W. Wilson, and R.G. Aspden, in "Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys," Editors: R.D. McCright, J. Slater, J. Hochmann and R. W. Staehle, (1977), NACE-Houston-U.S.A.
2. I.L.W. Wilson, and R.G. Aspden, Corrosion, 32, 193 (1976), NACE-Houston-U.S.A.
3. Ph. Berge, J.R. Donati, B. Prieux, and D. Villard, Corrosion, 33, 425 (1977), NACE-Houston-U.S.A.
4. R.S. Pathania, Corrosion, 34, 149 (1978), NACE-Houston-U.S.A.
5. J.R. Cels, Corrosion, 34, 198 (1978), NACE-Houston-U.S.A.
6. M.E. Indig, and N.J. Hoffman, Paper No. 135, Corrosion/77 Conference, NACE-Houston-U.S.A.
7. Y.S. Park, J.R. Galvele, A.K. Agrawal, and R.W. Staehle, Corrosion, in press, NACE - Houston - U.S.A.
8. Y.S. Park, A.K. Agrawal and R.W. Staehle, Corrosion, in press, NACE-Houston-U.S.A.