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Report COO-1319-27

A STUDY OF THE MECHANISM OF STRESS CORROSION
CRACKING IN THE IRON-NICKEL-CHROMIUM ALLOY SYSTEM

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U. S. ATOMIC ENERGY COMMISSION
Chicago Operations Office
Argonne, Illinois

Contract No. AT(11-1)-1319

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QUARTERLY

REPORT

By

THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION

1314 KINNEAR RD.
COLUMBUS, OHIO 43212

To U.S. ATOMIC ENERGY COMMISSION
Chicago Operations Office
Argonne, Illinois
Contract No. AT(11-1)-1319

On A STUDY OF THE MECHANISM OF STRESS
CORROSION CRACKING IN THE IRON-NICKEL-
CHROMIUM ALLOY SYSTEM

For the period 17 March 1965 - 16 June 1965

Submitted by R. W. Staehle, F. H. Beck, M. G. Fontana,
and J. P. Hirth
Department of Metallurgical Engineering

Date 9 July 1965

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I. INTRODUCTION

The aims of this program are (1) to evaluate systematically the susceptibility of iron-nickel-chromium alloys to stress-corrosion cracking in chloride- and hydroxide-containing environments, and (2) to establish a reliable model for stress-corrosion cracking in these alloys. The general experimental program is evaluating commercial and specially prepared alloys over the range of iron and nickel ratios and up to 40% chromium. Studies are being conducted in the areas of stress-corrosion experiments, electrochemistry, and physical metallurgy. Important objectives of this program are (1) to integrate the studies in the stress corrosion, physical metallurgy, and electrochemical areas; and (2) to conduct the studies with a high degree of self-consistency. Through this approach it is expected that the model for cracking which is eventually developed will have a high degree of credibility.

II. STRESS-CORROSION CRACKING EXPERIMENTS

A. RECIRCULATING AUTOCLAVE SYSTEM

During the past quarter several preliminary runs at 500°F and 600°F were made in the circulating system. The various components performed satisfactorily except for the mechanical joints in the preheater. These leaked during temperature cycling; therefore, it was decided that they should be welded. The welding should be completed during the first week in July.

B. SCOPING STUDIES OF ALLOY COMPOSITION

Results from a preliminary survey of stress corrosion cracking in various alloys are shown in Figs. 1-9. All specimens were 0.015" diameter wires. Conditions of experiments are generally described on each of the figures.

1. Cracking in Iron-Nickel-Chromium Alloys

Figure 1 shows photomicrographs from cracking of iron-chromium-nickel alloys. Cracking is observed in pure ternary alloys at nickel contents corresponding to that of Incoloy-800. Intergranular cracking is observed in alloys 33, 16, and 4B. Alloy 78 without fourth-component additions showed no cracking but the presence of molybdenum and nitrogen promoted cracking, as shown in Fig. 1. This effect of nitrogen and molybdenum appears to substantiate trends already observed at lower nickel contents by numerous other investigators.

The reasons for the intergranular cracking and the nitrogen and molybdenum effects are not known, and speculation is not appropriate at this point.

2. Effect of Fourth Components

Reasons for adding various fourth components have been discussed

Neg. # 362

Fig. 1 - Stress corrosion of iron-chromium-nickel alloys

in previous reports. Figure 2 summarizes metallographic observations of cracking caused by additions of fourth components to alloy 54 (Fe-15 Ni-20 Cr). Additions of metallic components were made at the 1.5 atomic per cent level and additions of non-metallics at 0.1 atomic per cent. Cracking occurred in all alloys containing fourth components. Contrary to the normal trend for the austenitic stainless steel to crack transgranularly, the alloys containing the platinum elements cracked intergranularly. The addition of rhenium also caused intergranular cracking. The effect of rhenium is interesting when compared with the trend observed in Fig. 3 for manganese additions. While the 1.5 atomic per cent Mn alloy in Fig. 2 cracked transgranularly, the commercial alloys, Type 202 and Tenelon, both exhibited some intergranular cracking. Manganese and rhenium are both in the same chemical family.

3. Commercial Stainless Steels

Figure 4 summarizes metallographic results of cracking in commercial stainless steels. Commercial stainless steels are being included in the study, along with the specially melted alloys, in order to provide information of direct engineering value.

4. NaOH Environments

Figure 5 summarizes the effect of 10% NaOH environment. Attack was similar on controls and test specimens and was intergranular for the alloys tested. Exposure to 1% NaOH, with and without oxygen over-pressure, for a 24-hour period at 600°F produced no observable attack.

5. Water + Oxygen + Chloride

Figure 6 compares results from exposure to water, water + oxygen, water + chloride, and water + chloride + oxygen at 600°F. It appears that the combination of both oxygen and chloride is necessary for the accelerated surface attack to occur.

6. Effect of Twin Interface

Figure 7 shows the effect of twin interface on direction of crack propagation. At the right in Figure 7 a transmission electron micrograph of an oxide film removed by bromine dissolution shows the progress of tunnels at the twin interface.

It appears that there is a definite effect of twin interface on crack propagation. When the crack crosses the twin interface, the angle of approach is approximately equal to the angle of leaving, i.e., the twin is a mirror plane. From other metallographic observations it is also clear that cracking does not always have this relationship to twin interfaces. Reasons for such behavior will be pursued in subsequent investigations of mechanisms of crack propagation.

The observed relationship between cracks and twin interfaces is a strong argument for the importance of defect structure to the mechanism of crack propagation.

Neg. # 368

Fig. 2 - Effect of fourth components on cracking of alloy 54(Fe-15 Ni-20 Cr)

Neg. # 367

Fig. 3 - Possible effect of manganese on the mode of cracking

Neg. # 365

Fig. 4 - Stress corrosion cracking of commercial stainless steels

Neg. # 364

Fig. 5 - Effect of NaOH environments

**COMBINED
CHLORIDE AND
OXYGEN
EFFECT**

**7 lb. load
24 hours
600 F
350 X**

**LEFT PHOTOS:
water + 0.1w/o Cl
+ 100 psi O₂**

**RIGHT PHOTOS:
water (typical of
chloride or
oxygen alone)**

Neg. # 360

Fig. 6 - Effect of various combinations of water, oxygen, and chloride

A-54

A-54 C

A-54

16-20

A-54 Be

16-20

Fe-20Cr-20Ni
(Paxton & Reed)

Fe-16Cr-20Ni-0.07 P
(Lang)

EFFECT OF TWIN INTERFACE ON CRACK PROPAGATION

600 F

0.1 W% NaCl

100 psi Oxygen overpressure

7 lb load

24 hours

As-Received T-304

boiling 42% MgCl₂ (Dean)

10,000 X

5000 X

Neg. # 366

Fig. 7 - Effect of twin interface on crack propagation

7. Accelerated Oxidation caused by Stress

Figures 8 and 9 show accelerated oxidation caused by stress. Non-stressed control specimens of the alloys shown in Figures 8 and 9 showed little attack. The complete oxidation of a 0.015" diameter wire represents an unusually large amount of oxidation for 600°F in a time period of 24 hours. The details of this stress-accelerated oxidation will be pursued at a later date as time permits.

III. MECHANICAL PROPERTIES

Tensile properties have been determined for selected alloys from room temperature to 1200°F and are summarized in Table I. Each temperature represents a single experiment. Multiple experiments were found to produce identical results. Wire specimens were 0.015" in diameter. The arrangement for hot tensile testing is shown in Figure 10 and the furnace in Figure 11. The furnace is a quick-opening type specially designed for obtaining high-temperature results as rapidly as possible. The specimen is protected by an inert atmosphere (argon). The tensile test is pulled as soon as test temperature is reached. An experiment to determine optimum holding time at temperature showed no change in properties between testing the moment test temperature was reached and after an approximately 15-minute holding time.

No comment on the data in Table I is appropriate at this time except to note the increase in strength properties with increasing chromium. All alloys were in the "as-drawn and strand-annealed condition."

Table II summarizes tensile results for alloys at 600°F. These data, together with those in the previous progress report, provide a complete picture of tensile data at room temperature and 600°F for all specially melted alloys in the as-received condition.

During the next reporting period the effect of annealing treatments will be evaluated and work will begin on completely characterizing the specially melted alloys in the dead soft condition.

IV. ELECTRON METALLOGRAPHY

Interactions of the environment and the metal surface are being studied using the following electron metallographic techniques.

1. Transmission Microscopy of Oxide Films

A preliminary study of commercial iron-chromium-nickel alloys was undertaken to determine the morphology of initial stages of stress corrosion cracking attack on alloys with varying nickel content. This early attack was studied using transmission electron microscopy of oxide films removed from specimens exposed to boiling $MgCl_2$. The technique used for obtaining the oxide film was similar to that of Nielsen.¹ The commercial alloys used were Type 304 (9% Ni), Type 309 (15% Ni), Type 310 (20% Ni), Incoloy-800 (32% Ni), Incoloy-825 (42% Ni) and Inconel-600 (77% Ni).

A 52 Be

A 54 S

**STRESS ACCELERATED
OXIDATION**
0.015" wire specimens
100 psi oxygen overpressure
.1 w/o NaCl
24 hrs
600 F
7 lb load

(stressed above,
non stressed below)

A 33

A 45

A 50 P

A 21 N

Neg. # 359

Fig. 9 - Accelerated oxidation. Comparison between stressed specimens and controls

Table I. Tensile Results of Selected Alloys (RT - 1200°F)

The specimens were tested under the following conditions:

Strain rate = 5 cm/min

Temperature as listed $\pm 10^\circ\text{F}$

Gage length = 7 inches

Yield strengths were determined at 0.2% offset

Alloy	Temperature (°F)	Tensile Stress (psi)	Yield Stress (psi)	% Elongation
#5 - (65 Fe-35 Ni)	Room Temp.	60,000	35,900	4.0
	200	55,750	27,700	20.8
	400	46,850	18,650	17.4
	600	44,000	16,950	18.5
	800	35,600	14,300	24.5
	1000	31,100	12,440	28.1
	1200	23,700	10,180	21.1
#8 - (35 Fe-65 Ni)	Room Temp.	80,000	27,650	30.3
	200	73,000	31,200	21.9
	400	74,000	24,000	26.7
	600	68,600	21,450	28.1
	800	52,750	18,500	19.7
	1000	41,400	13,000	19.1
	1200	33,600	16,800	7.9
#12 - (100 Ni)	Room Temp.	35,300	27,650	8.7
	200	29,900	21,450	5.6
	400	31,900	20,350	3.9
	600	27,900	23,200	7.3
	800	26,550	19,200	12.3
	1000	15,250	13,400	11.8
	1200	8,750	8,200	7.3
#29 - (80 Fe-10 Ni-10 Cr)	Room Temp.	40,800	12,750	10.7
	200	33,900	13,550	8.4
	400	29,650	15,250	9.5
	600	25,700	15,500	6.2
	800	24,300	15,200	6.2
	1000	18,800	11,450	5.6
	1200	9,450	8,600	1.7
#32 - (65 Fe-25 Ni-10 Cr)	Room Temp.	68,400	20,900	29.3
	200	59,000	18,650	23.6
	400	52,100	20,350	21.4
	600	50,500	16,650	20.8
	800	46,800	18,050	19.0
	1000	42,000	12,420	18.5
	1200	36,600	10,900	16.8

Table I. (Continued)

Alloy	Temperature (°F)	Tensile Stress (psi)	Yield Stress (psi)	% Elongation
#34 - (45 Fe-45				
Ni-10 Cr)	Room Temp.	60,300	20,900	22.5
	200	53,700	17,050	22.8
	400	46,500	20,000	16.0
	600	42,000	16,300	16.0
	800	41,750	17,100	16.0
	1000	38,500	12,900	20.8
	1200	33,300	10,300	18.0
#52 - (75 Fe-5				
Ni-20 Cr)	Room Temp.	81,900	25,850	26.5
	200	71,600	24,100	20.8
	400	68,800	24,600	23.6
	600	71,500	23,250	25.3
	800	69,500	21,950	25.0
	1000	59,600	17,800	23.6
	1200	50,800	15,850	18.8
#54 - (65 Fe-15				
Ni-20 Cr)	Room Temp.	76,550	24,300	42.0
	200	66,500	23,250	27.2
	400	58,200	22,900	22.2
	600	52,100	19,200	22.5
	800	47,500	17,225	18.5
	1000	42,700	16,400	15.2
	1200	33,700	13,950	10.7
#57 - (45 Fe-35				
Ni-20 Cr)	Room Temp.	73,750	27,300	35.7
	200	69,400	27,500	25.9
	400	63,600	25,500	23.4
	600	56,500	22,250	22.5
	800	55,800	20,600	20.8
	1000	50,250	18,720	18.5
	1200	44,000	16,150	16.0
#60 - (15 Fe-65				
Ni-20 Cr)	Room Temp.	89,500	32,200	28.1
	200	84,000	29,750	26.1
	400	79,700	27,600	25.0
	600	73,500	24,300	26.4
	800	72,500	24,900	26.7
	1000	64,700	22,600	25.3
	1200	53,300	19,750	18.0

Table I. (Continued)

Alloy	Temperature (°F)	Tensile Stress (psi)	Yield Stress (psi)	% Elongation
#62 - (80 Ni-20 Cr)	Room Temp.	84,500	31,000	11.0
	200	80,200	30,700	19.7
	400	79,600	29,200	20.2
	600	74,000	25,100	22.5
	800	72,500	25,300	23.0
	1000	64,700	23,300	23.0
	1200	54,750	19,750	18.0
#75 - (60 Fe-10 Ni-30 Cr)	Room Temp.	91,700	36,700	32.6
	200	82,500	32,800	28.6
	400	74,300	28,400	26.4
	600	68,100	24,700	24.7
	800	65,300	22,600	22.4
	1000	61,600	20,900	22.8
	1200	53,400	18,650	20.4
#90 - (60 Ni-20 Cr)	Room Temp.	114,000	47,800	35.4
	200	103,300	46,900	29.5
	400	95,750	41,500	30.6
	600	89,000	37,800	29.8
	800	87,250	35,000	31.0
	1000	83,400	36,700	31.1
	1200	68,750	33,300	22.2

Neg. # 274

Fig. 10 - Instron tensile machine and furnace arrangement

Neg. # 275

Fig. 11 - Water-cooled, quick-opening tensile furnace
(Marshall Products, Columbus, Ohio)

Table II. Tensile Results at 600°F

Alloy No.	Composition (atomic per cent)				Tensile Strength (psi)	Yield Strength (psi)	Elongation (%)
	Fe	Ni	Cr	Other			
4 B	70	30	--	--	39,200	21,600	18.3
5	65	35	--	--	44,000	16,950	18.5
6	55	45	--	--	48,300	18,550	20.2
8	35	65	--	--	68,600	21,450	28.1
12	--	100	--	--	37,900	23,200	7.3
13	95	--	5	--	62,200	59,300	1.26
14	90	5	5	--	86,100	82,000	1.40
15	85	10	5	--	38,500	17,300	23.1
16	80	15	5	--	41,250	20,900	21.2
17	75	20	5	--	76,700	66,300	5.4
18	70	25	5	--	105,600	91,500	1.68
19	65	30	5	--	101,000	90,500	1.40
20	55	40	5	--	40,650	13,000	23.3
21	45	50	5	--	46,900	12,400	19.1
21 Be	44.3	49.3	4.9	1.5 Be	71,200	20,300	23.8
21 Mo	44.3	49.3	4.9	1.5 Mo	59,300	22,000	23.5
21 N	45	49.9	5	.1 N	53,600	19,200	22.9
21 S	45	49.9	5	.1 S	31,100	63,300	21.2
24	15	80	5	--	61,600	18,550	22.6
29	80	10	10	--	25,700	15,500	6.22
32	65	25	10	--	50,500	16,650	20.8
33	55	35	10	--	49,700	17,500	19.2
34	45	45	10	--	42,000	16,300	2.85
41	75	10	15	--	100,500	77,900	15.4
42	70	15	15	--	48,900	15,800	24.4
43	65	20	15	--	48,500	16,400	21.9
45	55	30	15	--	43,800	19,200	19.2
46	45	40	15	--	52,500	16,400	21.1
48	25	60	15	--	65,000	21,800	23.7
50	8	77	15	--	62,200	20,300	21.0

Table II. (Continued)

Alloy No.	Composition (atomic per cent)				Tensile Strength (psi)	Yield Strength (psi)	Elongation (%)
	Fe	Ni	Cr	Other			
50 Al	7.9	75.8	14.8	1.5 Al	112,000	99,400	1.68
50 Be	7.9	75.8	14.8	1.5 Be	74,700	20,900	27.1
50 Mo	7.9	75.8	14.8	1.5 Mo	88,000	26,000	27.9
50 P	8	76.9	15	.1 P	87,000	35,800	24.0
50 S	8	76.9	15	.1 S	77,400	40,100	15.4
50 Ti	7.9	75.8	14.8	1.5 Ti	76,800	26,000	27.9
52	75	5	20	--	71,500	23,250	25.3
52 Be	73.9	4.9	19.7	1.5 Be	81,200	52,800	2.78
53	70	10	20	--	47,000	17,000	20.0
54	65	15	20	--	52,100	19,200	22.5
54 Al	64	14.8	19.7	1.5 Al	55,900	20,900	23.4
54 Au	64	14.8	19.7	1.5 Au	62,200	26,000	28.8
54 Be	64	14.8	19.7	1.5 Be	59,300	19,200	21.6
54 C	64.9	15	20	.1 C	53,200	21,400	20.1
54 Co	64	14.8	19.7	1.5 Co	54,200	17,500	22.5
54 Cu	64	14.8	19.7	1.5 Cu	54,200	18,600	25.4
54 Ir	64	14.8	19.7	1.5 Ir	59,450	24,000	26.2
54 Mn	64	14.8	19.7	1.5 Mn	52,000	20,900	21.0
54 Mo	64	14.8	19.7	1.5 Mo	58,500	22,200	24.7
54 N	64.9	15	20	.1 N	69,000	26,600	22.4
54 O	64.9	15	20	.1 O	52,700	24,000	19.7
54 P	64.9	15	20	.1 P	58,700	27,100	23.9
54 Pd	64.8	14.7	19.7	1.5 Pd	58,300	29,200	27.9
54 Pt	64	14.8	19.7	1.5 Pt	57,100	22,600	27.1
54 Re	64	14.8	19.7	1.5 Re	55,950	22,000	27.6
54 Rh	64	14.8	19.7	1.5 Rh	57,600	20,900	27.0
54 Ru	64	15.8	19.7	1.5 Ru	56,000	21,400	26.8
54 S	64.9	15	20	.1 S	55,300	30,500	27.4
54 Si	64	14.8	19.7	1.5 Si	57,800	21,400	18.0
54 Ti	64	14.8	19.7	1.5 Ti	64,400	22,600	23.7

Table II. (Continued)

Alloy No.	Composition (atomic per cent)				Tensile Strength (psi)	Yield Strength (psi)	Elongation (%)
	Fe	Ni	Cr	Other			
54 V	64	14.8	19.7	1.5 V	56,000	22,000	23.0
54 W	64	14.8	19.7	1.5 W	59,300	23,200	27.1
54 Zn	64	14.8	19.7	1.5 Zn	53,700	20,900	24.0
55	60	20	20	--	55,300	19,200	25.0
56	55	25	20	--	55,600	19,200	24.2
57	45	35	20	--	56,500	22,250	22.5
58	35	45	20	--	63,500	22,000	22.3
60	15	65	20	--	73,500	24,300	26.4
62	--	80	20	--	74,000	25,100	22.5
64	65	10	25	--	70,000	53,600	22.5
65	60	15	25	--	53,600	20,350	23.6
66	55	20	25	--	56,500	21,400	23.6
67	45	30	25	--	60,500	23,700	24.2
74	60	10	30	--	78,500	68,500	7.55
76	45	25	30	--	56,800	22,000	23.0
77	35	35	30	--	68,100	24,700	24.7
78	25	45	30	--	74,000	26,000	25.7
78 Be	24.6	44.3	25.6	1.5 Be	79,700	28,300	27.4
78 Mo	24.6	44.3	29.6	1.5 Mo	80,700	31,600	26.9
78 N	25	45	30	.1 N	90,800	19,500	24.6
78 S	25	45	30	.1 S	80,700	47,500	24.4
83	35	30	35	--	76,300	32,800	25.4
85	15	50	35	--	79,600	30,500	28.6
88	15	45	40	--	81,900	32,500	28.7
90	--	60	40	--	89,000	37,800	29.8
Haynes Alloy #25					134,500	59,900	56.0
Hastelloy N					109,500	42,000	39.7
" F					98,400	37,400	36.3
" C					109,400	59,700	19.5
Type 304 ELC					67,300	31,100	27.9

Table II. (Continued)

Alloy No.	Composition (atomic per cent)				Tensile Strength (psi)	Yield Strength (psi)	Elongation (%)
	Fe	Ni	Cr	Other			
304 W					64,400	30,500	27.9
Inconel 718					120,200	52,000	35.0
Incoloy 800							
(specially prepared)					49,450	18,630	20.2
Incoloy 800							
(commercial)					75,600	36,500	20.2
Type 430					73,500	50,800	10.0
Type 310					101,000	43,100	28.4
16 Cr-20 Ni					50,000	19,800	19.6
Type 202					88,200	33,900	29.0
Type 410					57,600	40,700	1.01
Type 308					68,400	29,400	25.2
Type 316 ELC					73,400	33,300	27.3
Type 316					69,100	39,400	27.0
Type 347					70,000	32,800	25.2
Type 309					83,600	35,000	26.0
Tenelon					95,500	43,500	39.0
Incoloy 825					94,000	39,800	24.7

Significant results from examination of the oxides replicas are summarized in Figures 12 and 13. Figure 12 shows general features of oxides from the various alloys. There appears to be a definite difference between relatively low-nickel and high-nickel alloys. In the lower nickel alloys twin boundaries and slip lines appear generally pronounced, and the background structure is definite and regular. In the higher nickel alloys the background structure is less regular and only the grain boundaries appear pronounced. Twins and slip lines are generally not evident.

Figure 13 summarizes observations of "tunnels." Tunnels are also evident in Figure 12. The actual three-dimensional nature of tunnels is verified using stereo pairs. Tunnels were found to occur at grain boundaries and twin interface, and within grains. The presence of tunnels was found at nickel contents as high as that in Incoloy-800.

Work is now starting to establish the range of alloy compositions over which the tunnels occur in the specially melted alloys.

2. Transmission Microscopy of Metal Films

Initial stages of environment-metal interaction are being studied by examining, with the electron microscope, thin films exposed to various environments. Thin films in the annealed, 5% strained, and strained and annealed conditions are being examined.

Figure 14 shows typical structures of fully annealed Alloy 54 (Fe-20 Cr-15 Ni). Note the general absence of dislocations except for one in the twin boundary of the lower figure.

Figure 15 shows typical structure observed in Type 309 stainless steel and in Alloy 54 after 5% strain.

Figure 16 shows typical structures in alloy 54 after 5% strain and aging at 1560°F for one hour.

Figure 17 shows typical chemical attack observed in Type 309 (prestrained 5%) stainless steel during electrochemical preparation of thin films. Attack appears generally to be along stacking faults.

Figure 18 shows typical attack which results from exposing Alloy 54 in the 5% prestrained condition to boiling acetic acid for 35 seconds. The buckling contours make it difficult to discern any of the details of structure with which attack is associated. However, the straightness of the fissures indicates some crystallographic dependence.

¹N. A. Nielsen, "I. Nature of Initial Corrosion of Stressed Austenitic Stainless Steel by Chloride Ions," Corrosion 20, (1964) 199.

Fig. 12 - Electron micrographs of surface oxides from various iron-chromium-nickel alloys

T 304 Annealed

T 310 As Received

Incoloy 800 Annealed

T 304 As Received

ELECTRON METALLOGRAPHY
10,000 X
Oxide Replicas By Bromine
Dissolution
Specimens Exposed To
Boiling 42% MgCl₂

Fig. 13 - Electron micrographs showing details of tunnels

Neg. 12-28

23,000X

Neg. 12-29

22,000X

Fig. 14 - Alloy 54(Fe-20 Cr-15 Ni) in the annealed condition

Neg. 10-10

24,000X

Neg. 9-9

27,000X

Fig. 15 - Typical structures in type 309 stainless steel (top) and alloy 54 (bottom) after 5% strain

Neg. 12-16 100,000X

Neg. 12-20 30,000X

Neg. 11-18 27,000X

Fig. 16 - Alloy 54 after 5% strain and aging 1560°F for one hour

Neg. S-4

10,000X

Neg. 9-1

13,000X

Fig. 17 - Preferential chemical attack in type 309 stainless steel (top) and alloy 54 (bottom) during electropolishing. 5% prestrain

Neg. 14-4

13,000X

Neg. 14-5

4,000X

Fig. 18 - Alloy 54 prestrained 54% exposed 35 seconds to boiling acetic acid

Figure 19 shows typical arrays of corrosion products in thin films of Type 309 stainless steel exposed to boiling magnesium chloride for 30 minutes. Subsequent work will extend these observations to other alloys, will determine orientation of the linear arrays, and will determine, if possible, any crystallinity of the corrosion product phase.

The arrays of corrosion products shown in Figure 19 appear to be crystallographically arranged. This is indicated by the change in direction at grain boundaries and by the linear and parallel nature of the arrays. The top left and bottom right photographs show corrosion products which outline the edge of the foil.

V. ELECTROCHEMICAL MEASUREMENTS

Electrochemical reactions are an integral part of all corrosion processes. It is anticipated that a study of the polarization behavior of Fe-Ni-Cr alloys will enhance our knowledge of the electrochemical process occurring during stress corrosion cracking. Electrochemical observations will be correlated with occurrences of stress corrosion cracking in the large autoclave system.

At this stage in the program numerous experimental techniques are being evaluated to find the most fruitful approach to the study of the stress corrosion cracking mechanism.

Initial work is being conducted in sulfuric acid because of the large amount of information already available on various iron-chromium-nickel alloys and because the sulfuric acid environment is relatively free of complex ions. During this phase of the investigation the active-to-passive transition exhibited by Fe-Ni-Cr alloys in slightly oxidizing environments will be determined. In addition, measurements can be made which are indicative of the stability of the passive films.

Secondly, work will be conducted in aqueous chloride solutions in which stress corrosion cracking occurs. In these solutions the effect of stress and alloy composition on the breakdown potential of passive films can be studied advantageously. An investigation of the effect of temperature, chloride concentration, and oxygen content of the chloride medium on pitting corrosion and on initiation of stress corrosion cracking sites will make an important contribution to mechanistic studies.

All electrochemical measurements are obtained by using the two-compartment pyrex glass cell shown in Fig. 20. The 500 and 150 ml capacity compartments, containing the anode and cathode, respectively, are separated by a fine-porosity, fritted-glass disk. Accommodations for an auxiliary electrode, a hydrogen electrode, and a thermometer are provided in the anode compartment. Before beginning each experiment, the cell is cleaned with a chromic-sulfuric acid solution and rinsed with triple-distilled water. Reagent grade sulfuric acid and triple-distilled water are used to prepare the electrolyte. Since trace amounts of organic impurities may be detrimental to potential measurements, the last distillation treatment is performed

38,000X

Neg. 15-17

12,000X

Neg. 15-9

23,000X

Neg. 15-16

23,000X

Neg. 15-24

22,000X

Neg. 15-18

18,000X

Neg. 15-30

Fig. 19 - Thin film of type 309 stainless steel exposed to boiling MgCl_2 for 30 minutes. Metal prestrained 5%

Fig. 20 - Pyrex glass cell used in electrochemical measurements

over alkaline permanganate. Hydrogen gas with an oxygen content of less than 1 ppm of oxygen is then dispersed through the electrolyte contained in both compartments of the cell for a 12-hour period. In addition to removing the oxygen from the cell, the solution is pre-electrolyzed for 12 hours by applying a potential of 2 volts across the cylindrical platinized platinum electrodes. Upon completion of the purification treatment the specimen is lowered into the electrolyte and its surface positioned immediately adjacent to the tip of the Luggin probe. To avoid possible contamination the probe is filled with solution syphoned from the anode compartment of the cell. The other end of the solution bridge is securely fastened to a bottle containing a saturated solution of K_2SO_4 which is interconnected by an agar bridge to a second bottle containing a saturated solution of KCl. A fine-fritted glass disk is used at the end of the probe to prevent excessive flow of the electrolyte from the cell. A saturated calomel electrode is placed in the second bottle. These precautions are taken to minimize the adverse effects of an unknown liquid junction potential.

The cell and all auxiliary components are immersed in a constant-temperature bath. To maintain uniformity of results the temperature is controlled to within one degree centigrade.

Specimen preparation is an integral and important part of any electrochemical experiment. A number of precautions are essential to ensure reproducible results. The following is a brief description of the method used in this program.

Cylindrical samples of annealed high-purity Fe-Cr-Ni alloys are carefully machined into 0.25-inch-diameter rods. A one-inch section of each rod is set into a specially prepared Teflon mount which holds the sample tightly. Electrical contact is achieved through an opening in the top of the mount into which one end of a stainless steel rod is inserted and fastened to the specimen. A thin Teflon jacket is slipped over the electrical lead and screwed into the Teflon housing, thereby providing a leak-proof seal. The entire electrode assembly is shown in Fig. 21.

The mounted specimen is then ground to a 600-grit finish through a series of metallographic papers just prior to the beginning of the experiment. Both cathodic and chemical activation treatments were tried, however, the latter proved more successful in rendering the surface active. The treatment consisted of a short 5-minute immersion in boiling 1N H_2SO_4 after which the electrode was assembled and immediately transferred to the cell.

A photomicrograph of the annealed Fe-20 Cr-15 Ni alloy is reproduced in Fig. 22.

All tests are conducted with the Model 4100 Research Potential Controller shown in Fig. 23. Current and potential measurements are plotted automatically on a Bristol Model 560 High-Speed (0.4 sec.) Dynamaster potentiometer recorder. This unique feature is achieved by employing a series of electrical relays, which, when connected to the Anotrol potential controller, provide a wide choice of potentiodynamic measurements. The significant characteristic of the experimental apparatus is its ability to record current over six orders of magnitude. Current resolution is 0.1 μ amp, whereas potentials may be read to within 1 mv if necessary.

Fig. 21 - Electrode assembly

Fig. 22 - Annealed Fe-20 Cr-15 Ni alloy

Fig. 23 - Measuring and control equipment for polarization studies

To illustrate the significance of electrochemical measurements on Fe-Ni-Cr alloys a representative anodic polarization diagram obtained by potentiodynamic methods is presented in Fig. 24. When the potential of the material is increased in the positive or noble direction starting from the open circuit equilibrium potential, the electrochemical response of the anode may be essentially divided into three areas of interest. These areas represent the active, passive, and transpassive behavior of the specimen. Briefly, the current density designated I_m corresponds to the maximum corrosion rate of the sample in the active range. In this region uniform and rapid dissolution of the material occurs. The point marked E_m signifies the potential at which the maximum current density is reached in the active range. With an additional increase in potential the material exhibits an active-to-passive transition. Conditions are thereby established which make possible the formation of a stable protective film on the exposed surface of the specimen. The film is continually undergoing dissolution and repair as indicated by the small but significant corrosion current, I_p , called the passive current density. The magnitude of the corrosion current and the potential range over which passivity exists is indicative of the stability of the film and is of utmost importance in systems employing anodic protection as a means of corrosion control. At higher potentials the passive film breaks down and the measured current increases. It is thought that the presence of Cr and Mo facilitate film dissolution. At still higher potentials a region of secondary passivity is obtained. This property is insignificant from a practical point of view, since the potential necessary to reach this stage is exceedingly high, as is the rate of metal dissolution. Oxygen evolution takes place above this potential region.

An experimental polarization curve of an Fe-20 Cr-15 Ni (Alloy 54) in 1N H_2SO_4 at 25°C is shown in Fig. 25. The areas previously discussed can be easily identified in this diagram. All potential measurements are reported with respect to the saturated calomel reference electrode. It may be noticed that a sharp decrease in current at high potentials is not shown in the diagram; however, a tendency toward secondary passivity is evident.

The diagram reproduced in Fig. 26 serves to illustrate the effect of scanning rate on the position of the anodic polarization curve. Current response is shown to vary over an order of magnitude, depending on the rate of increase in applied potential. The appropriate selection of the scanning rate is determined by the nature of the experimental program and the characteristics of the system being studied. Once a choice has been made, however, it is best to use it for the remainder of the investigation. Equally important is the temperature at which the experiment is conducted as shown in Fig. 27. The general shape of the curve remains constant; however, the rate of dissolution increases significantly with temperature. In Table III are given several of the values which are characteristic of the anodic response of Alloy 54 in 1N H_2SO_4 as a function of scanning rate and temperature.

SCHEMATIC POLARIZATION CURVE

Fig. 24 - Representative diagram of anodic polarization

Fig. 25 - Experimental polarization curve of an Fe-20 Cr-15 Ni alloy in 1N H_2SO_4 at 25°C

Fig. 26 - Effect of scanning rate on position of anodic polarization curves

Fig. 27 - Effect of temperatures on polarization curves

Table III. Corrosion of Fe-20 Cr-15 Ni Alloy in 1N H₂SO₄

Temperature, °C	pH	Scanning Rate, mv/min	Potential, mv (SCE)		Current Density, ma/cm ²	
			Open Circuit	Active	Active	Passive
25°	0.79	28.10	-400	-337	1.8	0.015
25°	0.79	84.40	-402	-315	14.7	0.039
25°	0.79	251.64	-411	-308	47.7	0.070
25°	0.79	28.10	-400	-327	1.8	0.015
50°	0.67	28.40	-421	-328	85.0	0.120
75°	0.46	28.15	-415	-320	293.0	0.400

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