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YAEC-67

YANKEE ATOMIC ELECTRIC COMPANY
RESEARCH AND DEVELOPMENT PROGRAM

STUDIES OF THE CORROSION OF AISI 304 STAINLESS STEEL AND AISI 4135 CARBON STEEL EXPOSED TO SATURATED SOLUTIONS OF BORIC ACID

R & D SUBCONTRACT NO.1 under
USAEC-YAEC CONTRACT AT (30-3)-222

NOVEMBER, 1958

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ATOMIC POWER DEPARTMENT
PITTSBURGH,30 P. O. BOX 355 PENNSYLVANIA

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Research And Development Program

STUDIES OF THE CORROSION OF AISI 304 STAINLESS STEEL AND AISI 4135 CARBON STEEL EXPOSED TO SATURATED SOLUTIONS OF BORIC ACID

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For The Yankee Atomic Electric Company
Under Research and Development Subcontract
No. 1 of USAEC-YAEC Contract AT(30-3)-222

November, 1958

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

I. ABSTRACT

AISI 304 stainless steel and AISI 4135 carbon steel specimens were exposed to five weight per cent (70°F) and thirteen weight per cent (140°F) boric acid solutions. These are essentially saturation concentrations. After four weeks exposure it was found that the AISI 304 stainless steel was not attacked under these conditions but that the carbon steel had developed considerable corrosion products in the form of scale. It was found that the attack on carbon steel at 70°F in a five weight per cent boric acid solution was greatly reduced by the addition of sufficient base to neutralize the solution. A thirteen weight per cent boric acid solution badly attacked the carbon steel at 140°F even when adjusted to neutral pH conditions.

II. INTRODUCTION

Concentrated boric acid solutions will be stored for use in the shutdown operation of the Yankee reactor. These solutions will be near saturation with respect to boric acid (H_3BO_3) and will be kept at temperatures of 130°F to 150°F in order to insure that the boric acid will be kept in solution.

The study herein reported was undertaken in order to obtain information on the corrosion behavior of stainless and carbon steels in boric acid solutions. This was to aid in the selection of materials of construction for storage vessels. The study was planned to span temperature conditions of storage. For this reason solutions of boric acid saturated at room temperature (approximately 70°F) and at 140°F were used. The boric acid saturation concentrations at these temperatures are 5 and 13% respectively. This first test was conducted under acidic conditions with no pH control.

Since it was probable that the Yankee reactor would operate at neutral or elevated pH, a second test was run under neutral conditions. Other conditions were similar to those of the acidic test except that pH was raised by the addition of base. Only carbon steel was studied under neutral conditions (with pH adjustment) since the stainless steel was essentially not attacked by the boric acid solution without pH adjustment.

III. CONCLUSIONS

A. AISI 304 stainless steel will adequately resist corrosion in saturated boric acid solutions at temperatures at least up to 140°F. Heliarc welds on AISI 304 stainless steel appear to resist corrosion in boric acid somewhat better than consumable electrode welds. However, neither type of weld showed significant corrosion.

B. AISI 4135 carbon steel is not a suitable container for highly concentrated boric acid solutions and is not recommended for use when exposure to saturated neutralized boric acid solutions at 140°F is required. Attack under these conditions is particularly severe at the weld zones. Carbon steel shows good corrosion resistance, however, in neutralized boric acid solutions at or below 70°F.

IV. PROCEDURE

A. Solution Preparation

Solutions for the tests were prepared from water of greater than 500,000 ohm-cm resistivity. Reagent grade chemicals were used. The procedures used for the acidic solution preparation was somewhat different from that used for the neutral solution.

1. Acidic Solution

The acidic saturated solutions were prepared by bringing the water to a temperature (95°F and 145°F respectively) slightly higher than test temperature in the presence of excess boric acid. The ambient temperature test solution was air cooled rapidly to 70°F with stirring, and decanted into 400 ml beakers. The 140°F test solution was held at 140°F overnight and rapidly decanted into beakers.

2. Neutral Solutions

The neutral solutions were prepared as follows. The calculated weight of H_3BO_3 for 5 and 13% solutions was measured. Only part of the required water was added since some water was to be added while adjusting the pH. The water was heated sufficiently to bring the boric acid into solution before the 10% KOH solution was added. After cooling to room temperature the pH was measured. When the pH was 7.3 (room temperature) the rest of the water was added. This did not affect the pH in either case. The solutions were then poured into the test beakers.

The amount of solution was just sufficient to cover about two thirds of the specimen, thus exposing about one third to the air and allowing the effects at the interface to be observed.

B. Specimen Preparation

The materials used in these tests were AISI 304 stainless steel and AISI 4135 carbon steel. Coupons were cut from 14 gauge rolled sheet. Certain coupons were cut, and weld joints made, using both consumable electrode and Heliarc welding techniques. The weld beads were exposed in both the ground and as-welded condition. All specimens were wet ground with 120 grit paper to remove scale before testing. Data on the specimens are shown in Table I. Similar types of specimens were given the same specimen number with an A suffix for acid conditions and a B suffix for neutral conditions, an an aid in comparing corrosion rates under these conditions. After sanding and grinding the specimens were measured to the nearest hundredth of a millimeter.

TABLE I - Carbon and Stainless Steel Specimen Data

Specimen Size 1 x 2 x 0.1 inch (nominal)

Material and Condition	Spec* No.	Initial Weight	Surface Area	Type of Specimen
Carbon Steel 70°F (Acidic)	17A	47.8013 g	43.0 cm^2	Consumable electrode weld, not ground
AISI 4135	19A	45.6080	43.6	Consumable electrode weld, ground
C 0.35%, Mn 0.73	21A	50.0169	48.8	Heliarc weld, weld not ground
Si 0.26, Cr 1.01	22A	47.4625	47.6	Heliarc weld, ground
Mo 0.20, Fe Balance	25A	47.4058	49.2	As rolled
	26A	49.1331	48.7	As rolled
Carbon Steel 140°F (Acidic)	18A	49.3034	44.3	Consumable electrode weld, not ground
	20A	46.9990	45.9	Consumable electrode weld, ground
	23A	51.9088	48.7	Heliarc weld, not ground
	24A	50.4743	48.3	Heliarc weld, ground
	27A	48.6657	47.6	As rolled
	28A	48.7704	43.9	As rolled
Stainless Steel	1	22.4183	27.6	Sensitized, 1200°F, 15 mins.
70°F (Acidic)	2	22.6911	27.7	Sensitized, 1200°F, 15 mins.
AISI 304	5	23.1917	28.5	As rolled
C 0.08%, Cr 19.30	6	22.6998	28.5	As rolled
Ni 9.15, Mn 1.12	9	23.7468	37.8	Consumable electrode weld, not ground
Si 0.37, S 0.02	11	28.6598	36.6	Consumable electrode wled, ground
P 0.04, Fe Balance	13	31.2911	37.2	Heliarc weld, not ground
	15	31.3806	28.2	Heliarc weld, ground
Stainless Steel	3	22.1878	27.6	Sensitized, 1200°F 15 mins.
140°F (Acidic)	4	21.9634	27.2	Sensitized, 1200°F 15 mins.
AISI 304	7	23.7468	28.9	As rolled
	8	23.3084	28.7	As rolled
	10	33.3077	37.2	Consumable electrode weld, not ground
	12	31.0547	38.0	Consumable electrode weld, ground
	14	31.4598	37.8	Heliarc weld, not ground
	16	30.2763	38.3	Heliarc weld, ground
Carbon Steel 70°F	17B	45.8255	42.9	Consumable electrode weld, not ground
(Neutral)	19B	43.9971	43.6	Consumable electrode weld, ground
AISI 4135	21B	48.0023	48.7	Heliarc weld, not ground
	22B	45.4724	47.5	Heliarc weld, ground
	25B	45.5390	49.3	As rolled
	26B	46.6886	49.0	As rolled
Carbon Steel 140°F	18B	43.4635	44.4	Consumable electrode weld, not ground
(Neutral)	20B	40.7144	46.0	Consumable electrode weld, ground
AISI 4135	23B	45.8631	48.6	Heliarc weld, not ground
	24B	44.0693	48.2	Heliarc weld, ground
	27B	44.2427	47.6	As rolled
	28B	44.4188	44.0	As rolled

* To aid in making comparisons, similar types of specimens were given the same number in different tests.

Before testing the specimens were degreased and cleaned by a series of rinses made in the following order:

1. 1% Alconox
2. acetone
3. trichloroethylene
4. acetone
5. demineralized water.

The specimens were dried to obtain a consistent weight before weighing. It was necessary to dry the carbon steel rapidly to prevent rusting. This was accomplished in an oven kept at 230°F. The specimens were transferred to a desiccator for cooling. When cool the specimens were weighed to the nearest 0.1 mg.

After placing the specimens in individual beakers the test solution was added and loose fitting covers placed on the beakers (glass covers were used on 140°F test beakers). The 140°F test was conducted in an oven and the ambient temperature test was conducted in a storage cabinet.

C. Test Schedule

Daily examinations of the solutions and specimens were made. Changes in appearance of either were noted. The addition of demineralized water was required about every other day in the solutions kept at 140°F due to evaporation losses. About 30 ml of freshly demineralized water was added each time to each test beaker to maintain the proper dilution of boric acid.

After two and four weeks exposure under acidic conditions and after two, four and eight weeks exposure under neutral conditions, the specimens were removed from the solutions and rinsed free of adherent scale by alternate spraying and soaking in demineralized water. The specimens were then dried and weighed. After photographing the specimens and taking ten milliliter samples of the test solutions the specimens were returned to their respective solutions.

The solutions samples (10 ml from each beaker of solution) taken from identical tests were mixed to obtain an average analysis since all materials were identical in composition.

The temperature variations occurring in the 140°F tests were small. The test was conducted in a convection oven, which was held at 140 ± 5°F. The ambient temperature varied considerably. The acidic test was conducted in the range of 70° + 20°, - 15°F. The neutral test temperature range was 70° + 5°, - 15°F.

V. RESULTS

A. Acidic Test

The acidic corrosion test was terminated after four weeks because of extensive scale formation and sedimentation of a yellow iron salt in the carbon steel test solutions. Yellowing of the 140°F carbon steel test solutions began within the first eight hours. The ambient temperature test solutions also yellowed but at a slower rate and the yellowing was not noticed until about 24 hour's had elapsed. There was no discoloration of the solutions exposed to the stainless steel.

The solutions held at both temperature developed crystals. This was believed to be due to evaporation loss of solvent in the high temperature case. It was probably due to decreasing ambient temperatures in the second case. The solutions were saturated at 70°F and 140°F respectively at the start of the test.

Within two days after the start of the 140°F test, scale began forming on the specimens of carbon steel at the liquid-air interface.

Scale formation on the ambient temperature carbon steel test coupons was seen at the interfacial area at the end of the first two weeks. Figure 1 shows the appearance of the carbon steel at the end of the four week test. The weld zones of the carbon steel (ground and unground) were attacked to a greater degree than was the base metal. Figure 2 shows the stainless steel specimens after the same exposure time with no stain or other attack being evident.

Table II shows the weight change information obtained. Note that there was no significant attack on the stainless steel during acidic exposure except on the consumable electrode welded specimens tested at 140°F.

In all cases the weight changes for stainless steel are relatively insignificant as shown in the summary in Table III.

The corrosion rates on carbon steel under acidic conditions, particularly at 140°F (Table III) are somewhat high. At ambient temperatures the carbon steel attack rate would not be a problem except for the development of scale which is hard and brittle and readily flakes off. This condition could lead to clogging of the injection system by the lodging of flakes in the system's valves and pumps. The iron content of the test solutions (140°F) was about 2% after four weeks exposure. Most of this was in the form of a voluminous yellow flocculent material.

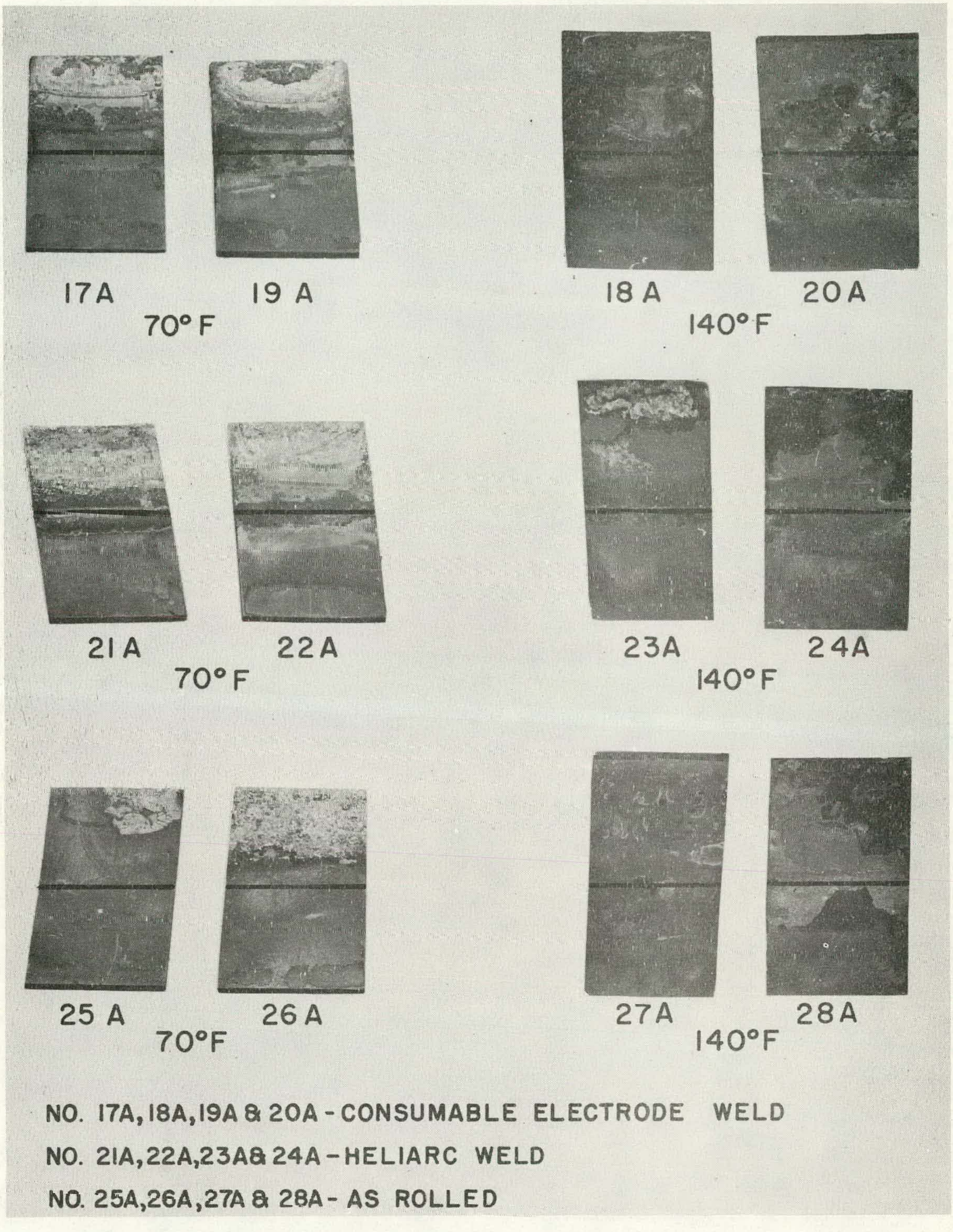

Figure 1

AISI 4135 Carbon Steel After 4 Weeks Exposure in Saturated Boric Acid. Black Line Indicates Approximate Air-Water Interface on Specimens. Air Exposure Is Above Line While Water Exposure Is Below Line.

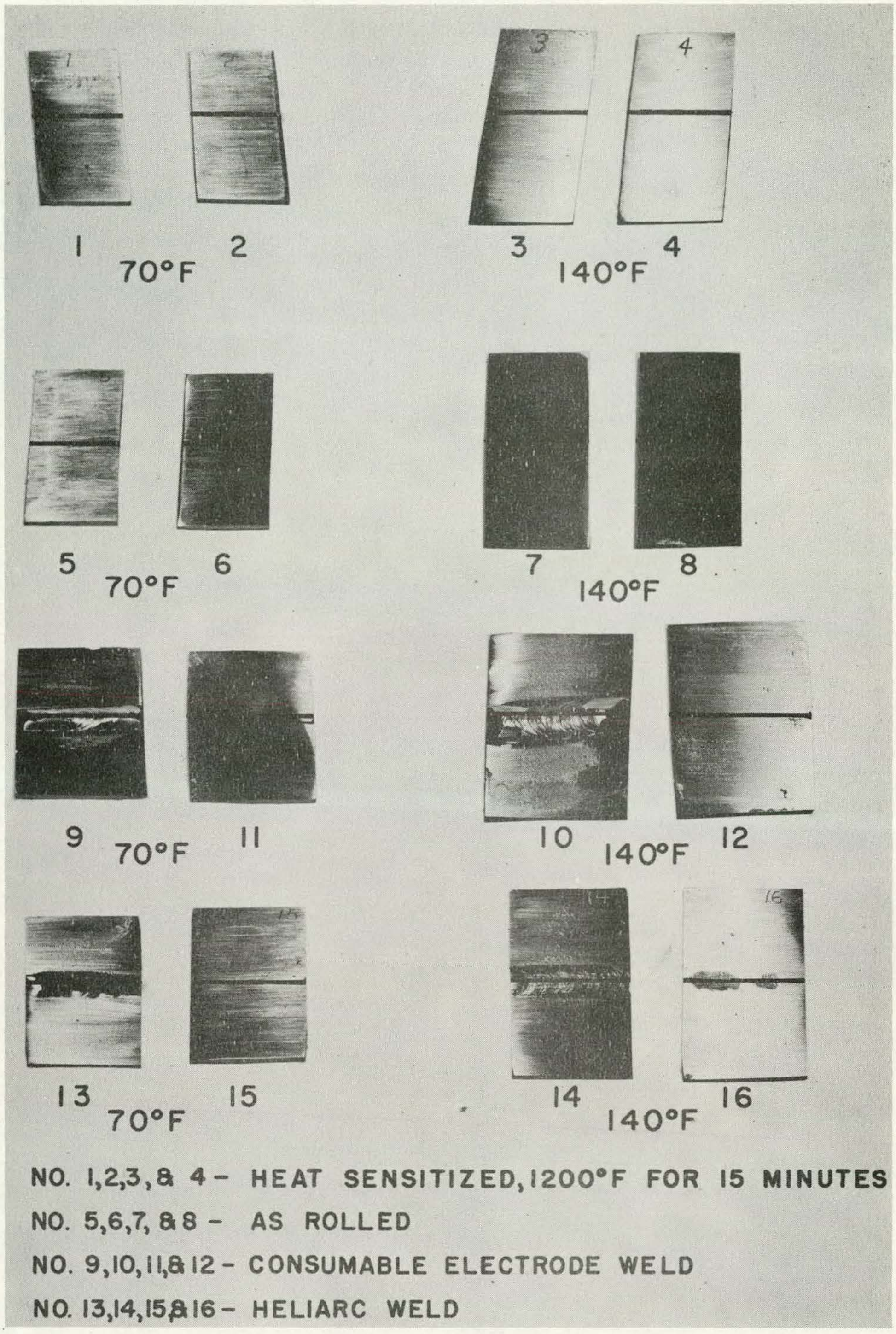

Figure 2

AISI 304 Stainless Steel After 4 Weeks Exposure in Saturated Boric Acid. Black Line Indicates Approximate Air-Water Interface on Specimens. Air Exposure Is Above Line While Water Exposure Is Below Line.

TABLE II

Weight Change of Carbon and Stainless Steel During Acidic Exposure

Material	Specimen No.	Cumulative Weight Change Two Weeks	Cumulative Weight Change Four Weeks
Corrosion in Saturated Boric Acid Solution at 70°F:			
Stainless Steel: AISI 304	1	- 0.7 mg/dm^2	0 mg/dm^2
	2	- 0.4	+ 1.1
	5	- 0.4	+ 0.7
	6	- 0.4	+ 0.7
	9	(- 6.6)	(- 6.9)
	11	0	- 0.3
	13	- 1.6	- 1.1
	15	0	+ 0.5
Carbon Steel: AISI 4135	17A	- 616	- 1032
	19A	- 614	- 983
	21A	- 532	- 860
	22A	- 560	- 903
	25A	- 414	- 623
	26A	--	- 636
Corrosion in Saturated Boric Acid Solution at 140°F:			
Stainless Steel: AISI 304	3	0	0.4
	4	0	0.4
	7	0	0
	8	0	- 0.3
	10	- 12.9	- 19.6
	12	- 9.7	- 13.9
	14	- 2.6	- 3.2
	16	0.3	- 0.3
Carbon Steel: AISI 4135	18A	- 3680	- 6370
	20A	- 4290	- 7890
	23A	- 3350	- 7000
	24A	- 4470	- 7000
	27A	- 2180	- 3890
	28A	- 2300	- 4240

TABLE III

Average Corrosion Rates of Carbon and Stainless Steels

Corrosion rates are averaged for comparison only. Rates decreased with time except as noted.

	Average Corrosion Rates 70°F	140°F
STAINLESS STEEL (ACIDIC TEST)		
Consumable Electrode Weld	Nil	7×10^{-4} in/yr
Heliarc Weld	Nil	Nil
Sensitized	Nil	Nil
As Rolled	Nil	Nil
CARBON STEEL (ACIDIC TEST)		
Consumable Electrode Weld	6×10^{-3} in/yr	4.3×10^{-2}
Heliarc Weld	5×10^{-3}	4.2×10^{-2}
As Rolled	4×10^{-3}	2.4×10^{-2}
CARBON STEEL (NEUTRAL TEST)		
Consumable Electrode Weld	5.7×10^{-6}	140°F Weight loss increased exponentially with time.
Heliarc Weld	1.2×10^{-6}	
As Rolled	3.2×10^{-5}	

B. Neutral Test

The corrosion of the AISI 4135 carbon steel specimens was confined in both cases (70°F and 140°F) to the interface region. There was no change in appearance until the fifth week when the 140°F test coupons began to noticeably darken in the areas exposed to the neutral pH solution of boric acid.

Metallographic examinations of the specimens exposed to neutral pH solutions of boric acid maintained at room temperature were made (see Figure 3). There was no visible attack up to 450X magnification. The room temperature test solutions remained bright and clear except for some yellowing of crystals near the end of the test. The crystals formed near the end of the second week and probably represent precipitation of boric acid caused by either loss of water due to evaporation or temperature decrease.

Figure 4 shows the appearance of a Heliarc weld zone after 8 weeks exposure at 140°F, in which excessive corrosion of heat affected areas was observed. Figure 5 shows that there was some attack on the base metal at 140°F. The 140°F solutions also showed crystal formation presumably due to evaporation. (It was noted that the pH rose slightly as precipitation of crystals occurred.) These crystals yellowed slightly during the second week. The 140°F solutions were quite dark at the end of the eighth week. About 1 ppm of iron was found suspended in a composite 140°F sample versus about 0.3 ppm iron in the ambient temperature sample taken at the conclusion of the test.

Weight change information is shown in Table IV. Note that the weight change of carbon steel at 140°F increases exponentially with time. This confirms the accelerated attack observed during the final weeks. The weight changes found on the samples exposed at 70°F indicate a much reduced rate of attack, also confirming visual and microscopic observations. Penetration rates that were averaged for the eight week period for purposes of comparison are shown in Table III.

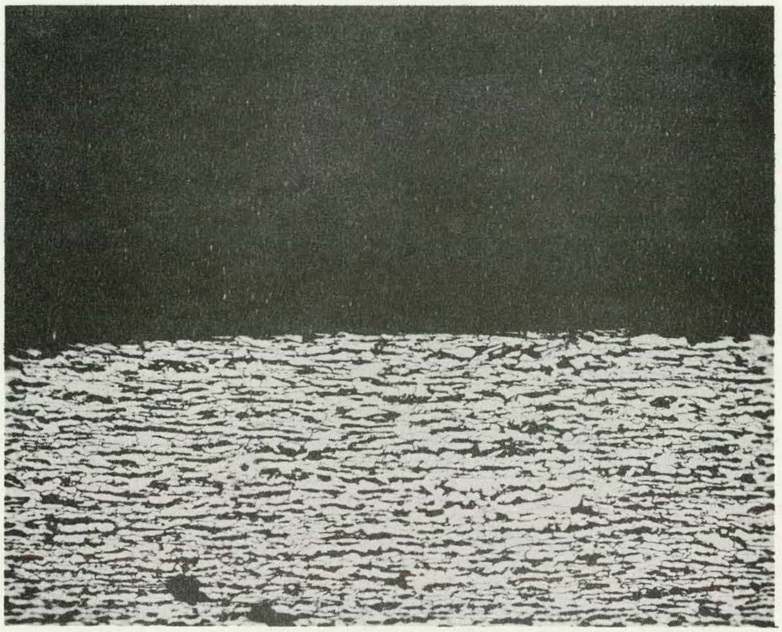

Figure 3

Photomicrograph (250X) of AISI 4135 Carbon Steel Specimen After 8 Weeks Exposure to a Neutral pH Solution of Boric Acid at 70°F. (No attack on the interface area)

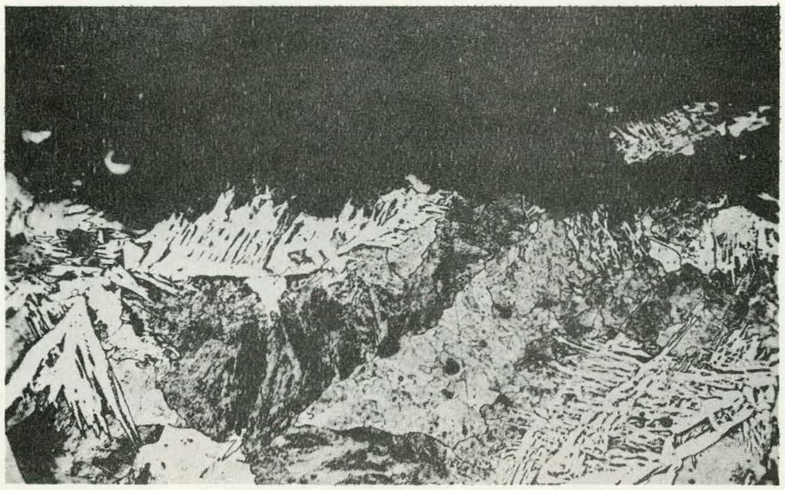

Figure 4

Photomicrograph (250X) of AISI 4135 Carbon Steel Weld Zone After 8 Weeks Exposure to a Neutral pH Solution of Boric Acid at 140°F. (Pitting of the weld zone)

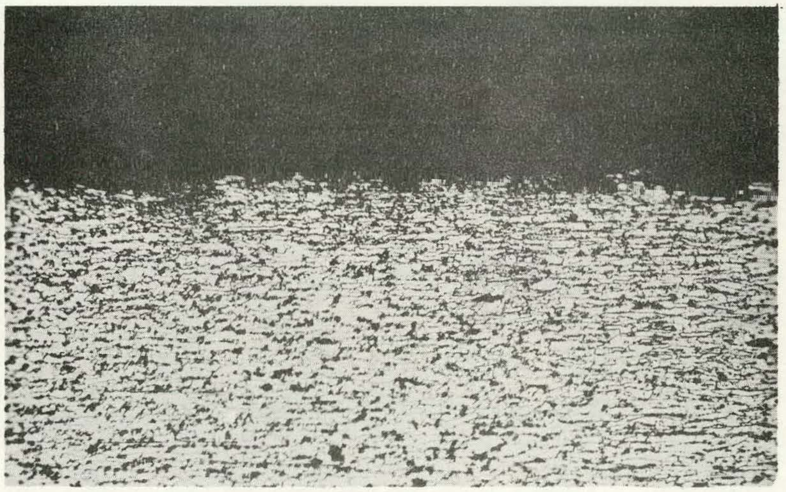

Figure 5

Photomicrograph (250X) of AISI 4135 Carbon Steel Specimen After 8 Weeks Exposure to a Neutral pH Solution of Boric Acid at 140°F.

TABLE IV

Weight Change of Carbon Steel After Exposure to Neutral pH Solutions of Boric Acid

Corrosion Found When Carbon Steel was Exposed to Saturated Boric Acid Solutions with pH control.

Specimen No.	Cumulative Weight Change After		
	2 weeks	4 weeks	8 weeks
70°F			
17B	- 0.9 mg/dm^2		- 2.5 mg/dm^2
19B	- 0.2		- 1.6
21B	- 3.1		- 2.5
22B	- 1.1		- 5.5
25B	- 1.8		-10.1
26B	- 0.8		- 9.4
140°F			
18B	- 5.2	- 118.5 mg/dm^2	- 2432
20B	- 9.8	- 124.8	- 1180
23B	- 0.4	- 116.0	- 1313
24B	- 0.6	- 133.6	- 1297
27B	- 0.8	- 36.6	- 1025
28B	- 0.7	- 7.5	- 1157