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CORROSION OF STAINLESS STEEL IN HNO_3-HF SOLUTIONS

by

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ABSTRACT

Solutions of HNO_3-HF for dissolving power reactor fuel elements can be handled safely in 304L and 309SCb stainless steel equipment under carefully controlled conditions. The corrosion behavior of both wrought and welded 304L and 309SCb was investigated in various HNO_3-HF solutions, ranging in HNO_3 concentration from 0 to 10.0M and HF concentration from 0.01 to 1.5M, and at temperatures from 24°C to the boiling point.

CONTENTS

LIST OF TABLES AND FIGURES

CORROSION OF STAINLESS STEEL IN HNO_3-HF SOLUTIONS

INTRODUCTION

Irradiated fuel elements from power reactors may be processed in the separations facilities at the Savannah River Plant. Since some of these elements are clad with zirconium or Zircaloy, process solutions containing a low concentration of HF in HNO_3 have been proposed for the codissolution of the cladding and the uranium alloy or oxide core. The addition of HF to the process solutions introduces a corrosion problem with the existing stainless steel equipment.

This report is a summary of the corrosion behavior of stainless steel in various HNO_3-HF solutions, ranging in HNO_3 concentrations from 0 to 10.0M and HF concentrations from 0.01 to 1.5M, at temperatures from 24°C to the boiling point. Since most of the process equipment is Type 304L or 309SCb, the corrosion behavior of these steels in both the wrought and welded form was investigated.

SUMMARY

Solutions of HNO_3-HF can be handled safely in 304L and 309SCb stainless steel process equipment, if the conditions are carefully controlled.

Some general conclusions from this study of the corrosion behavior of stainless steel in HNO_3-HF are:

1. The corrosion resistance of wrought 309SCb is superior to that of wrought 304L.

2. The corrosion resistance of 304L welded with 308L filler rod is equal to that of wrought 304L.

3. Reducing the HNO_3 concentration from 3.0 to 1.0M in a boiling 0.075M HF solution reduces the corrosion rate of 309SCb welds from 630 to 25 mpy.

4. In boiling HF solutions that do not contain HNO_3, both wrought and welded 309SCb corrode at about the same rate. Grey films form on the corrosion coupons, which result in a pitting type of attack.

5. Additions of 0.05 - 1.0M HNO_3 to boiling HF solutions decrease the corrosion rate of both wrought and welded 309SCb from that obtained in the HF solutions and convert the pitting attack to uniform corrosion. Increasing the concentration of HNO_3 above 3.0M increases the corrosion rate of 309SCb above that observed for straight HF solutions.

6. Welds made with 309SCb filler rod corrode intergranularly at a high rate in boiling solutions above 3.0M HNO_3 and 0.075M HF. This intergranular corrosion is due to chemical attack of the columbium carbide particles precipitated in a continuous network throughout the weld.

7. At least 1 mole of aluminum per mole of fluoride is required to reduce the corrosion rate to an acceptable level for welded 309SCb in boiling 0.075M HF solutions above 3.0M HNO_3. At higher HNO_3-HF concentrations even greater aluminum-to-fluoride ratios are required.

8. Annealing 309SCb welds for 30 minutes at 1950°F and water quenching decreases the corrosion rate of the weld to almost that of wrought 309SCb.

9. Welds of 308L are equal in corrosion resistance to wrought 309SCb.

10. "Knifeline" attack occurs in 309SCb base metal adjacent to a weld, because of chemical attack on the columbium carbide particles that are precipitated at the grain boundaries by the heat of the weld.

DISCUSSION

CORROSION TEST PROCEDURE

Conventional gravimetric corrosion test procedures were used. Tests were conducted at 24, 40, 60°C, and the boiling point, with both wrought and welded coupons. Each sample was tested for five 48-hour periods, the corrosion rate for each sample was calculated after each 48-hour test, and the five tests were averaged. The corrosion rate for each test condition was determined by averaging the rates of the samples exposed to the solution. Generally, three samples were tested in each solution.

Since preferential weld attack occurred in some solutions, weld corrosion rates were estimated by the following method. The product of the per cent wrought area times the wrought corrosion rate was subtracted from the coupon corrosion rate. Then, the difference was divided by the per cent weld area to estimate the "weld corrosion rate".

Prior to corrosion testing, all samples were ground to a 120-grit finish. Then the samples were measured and the surface area was calculated. After the coupons were degreased in acetone, they were weighed on a precision balance to five decimal places.

At temperatures below the boiling point, tests were conducted in "Saran" pipe sections in a constant-temperature water bath. "Teflon"-lined spool pieces were used for tests at the boiling point. All coupons were supported on "Teflon" sample holders. About 40 ml of solution was provided per square inch of sample.

CORROSION OF WROUGHT AND WELDED 304L

Type 304L stainless steel was studied in a variety of HNO_3-HF solutions at temperatures from 24°C to the boiling point. In all cases the corrosion resistance of 304L welded with 308L filler rod was equal to wrought 304L. The corrosion resistance of the 308L weld was superior to the wrought 304L base metal. Characteristically, the corrosion of 304L in HNO_3-HF was uniform, not intergranular or pitting corrosion. Table I summarizes the corrosion data.

EFFECT OF HNO_3-HF CONCENTRATION AND TEMPERATURE

In HNO_3 solutions the corrosion rate of 304L is below 5 mpy at concentrations ranging from 0 to 50% HNO_3 and at temperatures up to the boiling point.[1] However, very small additions of HF to HNO_3 solutions rapidly increase the corrosion rate of 304L to an excessive level. Figure 1 contains isocorrosion curves at several constant temperatures, which show the effect of varying the HNO_3 and the HF concentration on the corrosion rate of 304L. Generally, the corrosion rate increased as a logarithmic function of the HF concentration up to 1.5M HF. At 60°C and below, the corrosion rate of 304L decreased with an increase in HNO_3 concentration at a given HF concentration. However, at the boiling point, an increase in HNO_3 concentration increased the corrosion rate at a given HF concentration. Increasing the temperature of the HNO_3-HF solutions accelerated the corrosion rate.

Since the processing of power reactor fuels would be an intermittent or batch process, an initial corrosion rate of about 50 mpy would probably be acceptable. Under these conditions the following solutions could be contained in 304L equipment.

Temperature below 24°C:	HF	0.3M
	HNO_3	2.0-10.0M
Temperature below 40°C:	HF	0.15M
	HNO_3	2.0-10.0M
Temperature below 60°C:	HF	0.07M
	HNO_3	2.0-10.0M
Temperature at boiling:	HF	0.001M
	HNO_3	2.0-6.0M

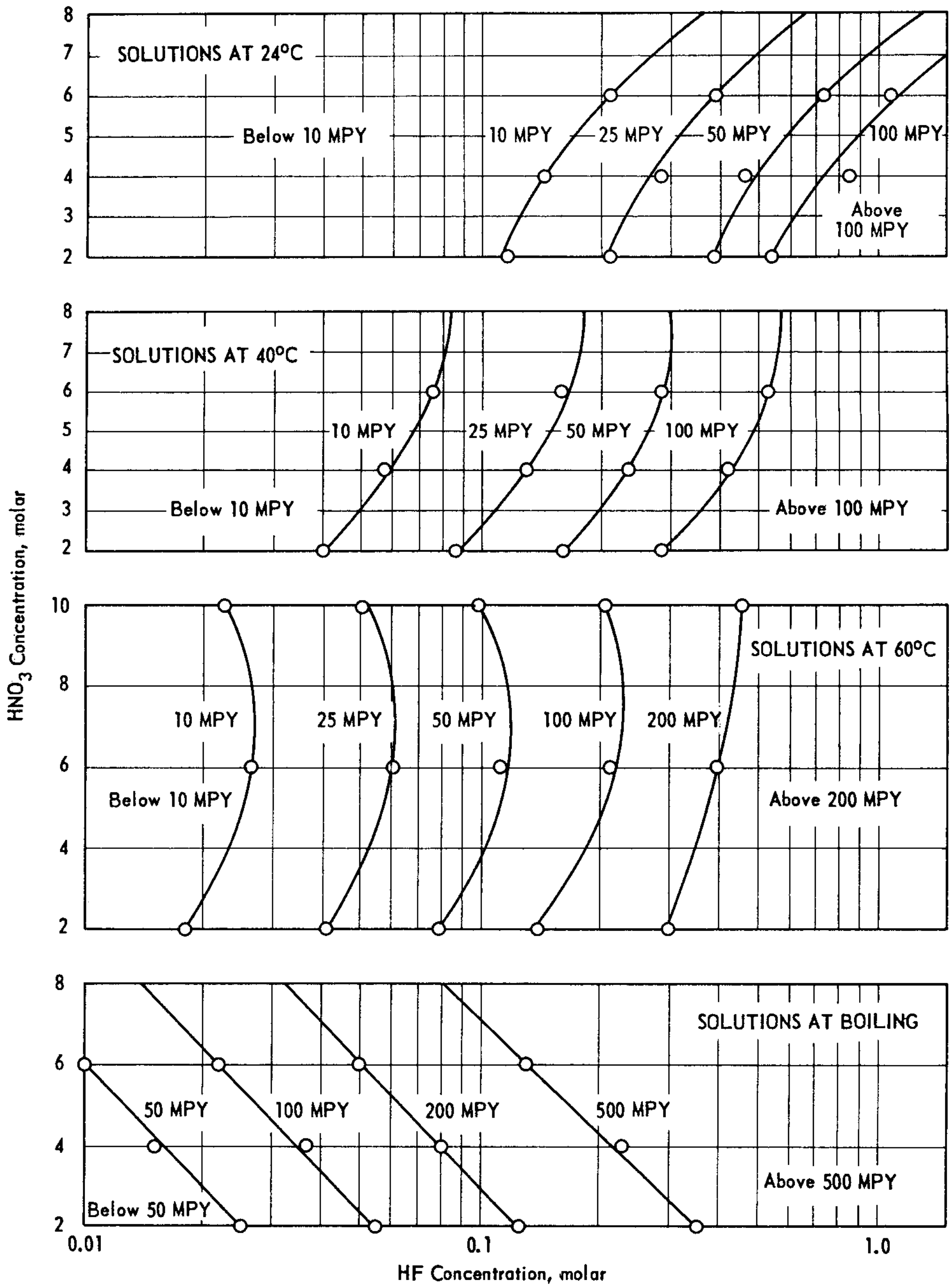


FIG. 1 CORROSION OF 304L IN HNO_3-HF SOLUTIONS

EFFECT OF ZIRCONIUM AND URANIUM

In processing zirconium- and Zircaloy-clad power elements, the 304L equipment would only be exposed to pure HNO_3-HF solutions in the initial stages. Therefore, the effect of zirconium and uranium in HNO_3-HF solutions on the corrosion rate of 304L was studied at 60°C. Results are reported in Table II and plotted in Figure 2.

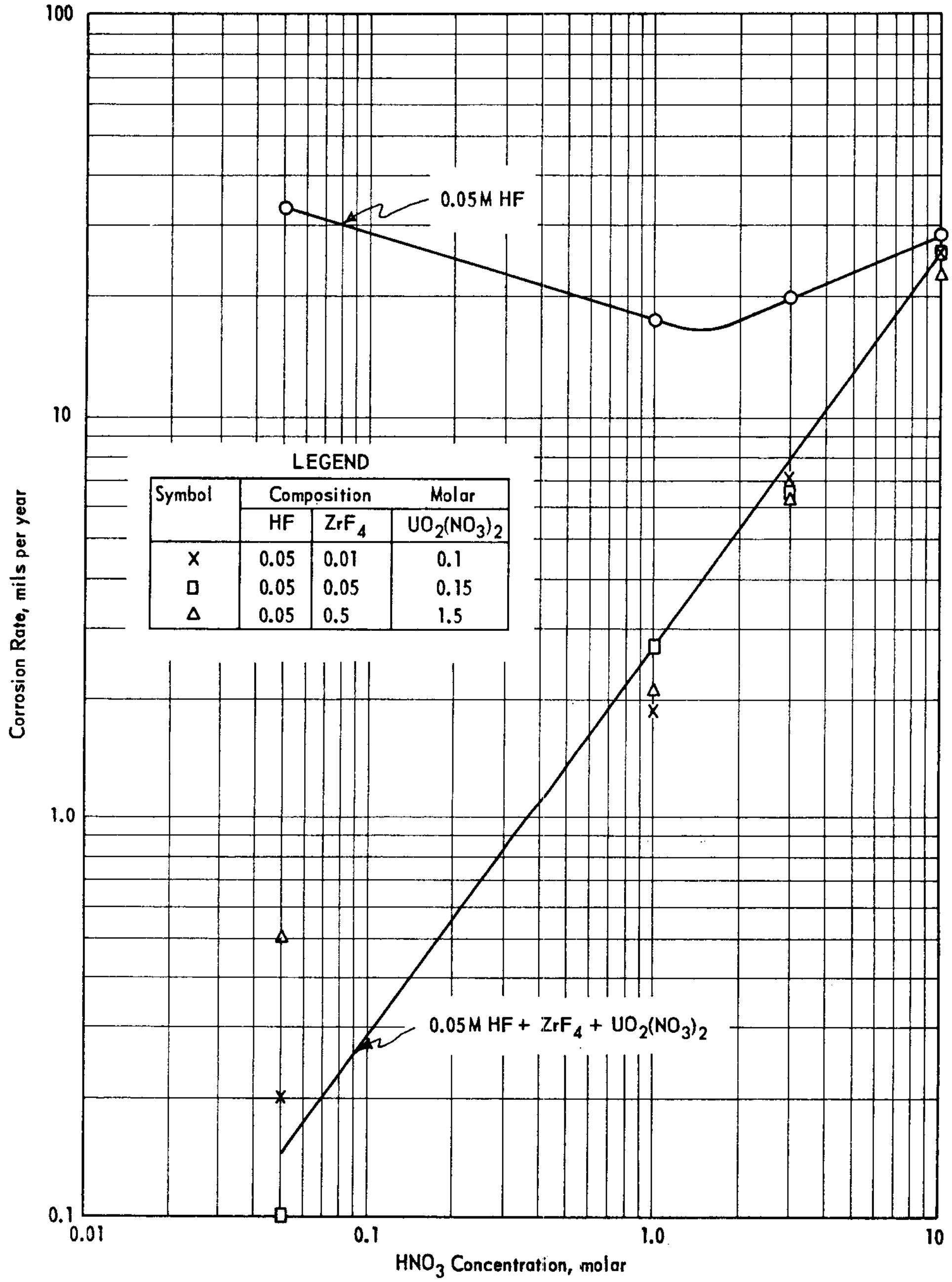


FIG. 2 CORROSION OF 304L STAINLESS STEEL IN HNO_3-HF-Zr-U SOLUTIONS AT 60°C

In control solutions of 0.05M HF the addition of up to 3.0M HNO_3 decreased the corrosion rate. Addition of ZrF_4 and $UO_2(NO_3)_2$ to HNO_3-HF solutions decreased the corrosion rate of 304L. Approximately equal corrosion rates were obtained in HNO_3-HF solutions containing the following combinations of ZrF_4 and $UO_2(NO_3)_2$.

Solution Composition, M	
ZrF_4	$UO_2(NO_3)_2$
0.01	0.1
0.05	0.15
0.5	1.5

This was attributed to the fact that ZrF_4 tended to increase the corrosion rate, while $UO_2(NO_3)_2$ tended to decrease the corrosion rate of 304L in HNO_3-HF solutions. The ZrF_4 hydrolyzed in the acid solutions to give additional free fluoride; $UO_2(NO_3)_2$ hydrolyzed to give additional nitrate, which inhibited corrosion.

Concentrations of 0.5M ZrF_4 and 1.5M $UO_2(NO_3)_2$ did not dissolve completely in HNO_3-HF solutions at room temperature.

EFFECT OF ALUMINUM

Aluminum effectively complexed fluoride and reduced the corrosion rate of stainless steel in HNO_3-HF solutions. Table III summarizes the effect of $Al(NO_3)_3$ on the corrosion of 304L. The corrosion rate was decreased to acceptable levels when the aluminum-to-fluoride ratio was 1:3.

CORROSION OF WROUGHT 309SCb

In HNO_3-HF solutions the corrosion resistance of 309SCb was superior to 304L. Table IV summarizes the corrosion data for 309SCb in various HNO_3-HF solutions at temperatures from 24°C to boiling.

EFFECT OF HNO_3-HF CONCENTRATION AND TEMPERATURE

The corrosion rate of 309SCb increased with an increase in HF concentration. Above a concentration of 1.0M, increasing the HNO_3 concentration increased the corrosion rate of 309SCb. However, the addition of up to 1.0M HNO_3 to boiling HF solutions above 0.05M HF decreased the corrosion rate of 309SCb. The following table illustrates these effects of HNO_3 at constant HF concentrations.

Corrosion Rates of 309SCb in Boiling HNO_3-HF Solutions

Solution Composition, M		Corrosion Rate, mpy		
HNO_3	HF	Vapor	Interface	Liquid
0.05	0.05	2.5	3.1	3.1
1.0	0.05	3.5	5.4	5.1
3.0	0.05	12	15	15
10.0	0.05	114	139	146
0.05	0.25	57	64	81
1.0	0.25	35	37	38
3.0	0.25	38	46	63
10.0	0.25	251	367	506
0.05	1.0	177	335	259
1.0	1.0	145	103	92
3.0	1.0	117	349	339
10.0	1.0	574	1042	1115

Another conclusion that may be drawn from this data is the fact that the corrosion rate was highest in the liquid phase. No preferential interface or vapor phase corrosion was observed on the test samples. In solutions containing both HNO_3 and HF, uniform corrosion occurred. However, in HF solutions alone pitting occurred. As little as 0.05M HNO_3 in HF solutions was sufficient to convert this pitting attack to uniform corrosion.

Increasing the temperature of the HNO_3-HF solutions increased the corrosion rate of 309SCb. Figure 3 contains isocorrosion curves for varying HNO_3-HF concentrations at several constant temperatures.

Under dissolving conditions with the temperature at the boiling point, the following HNO_3-HF solutions could be contained in a wrought 309SCb dissolver, assuming an initial corrosion rate of 50 mpy as acceptable.

Solution Composition, M	
HNO_3	HF
4.0	0.05
4.0	0.075
4.0	0.1
1.0	0.5

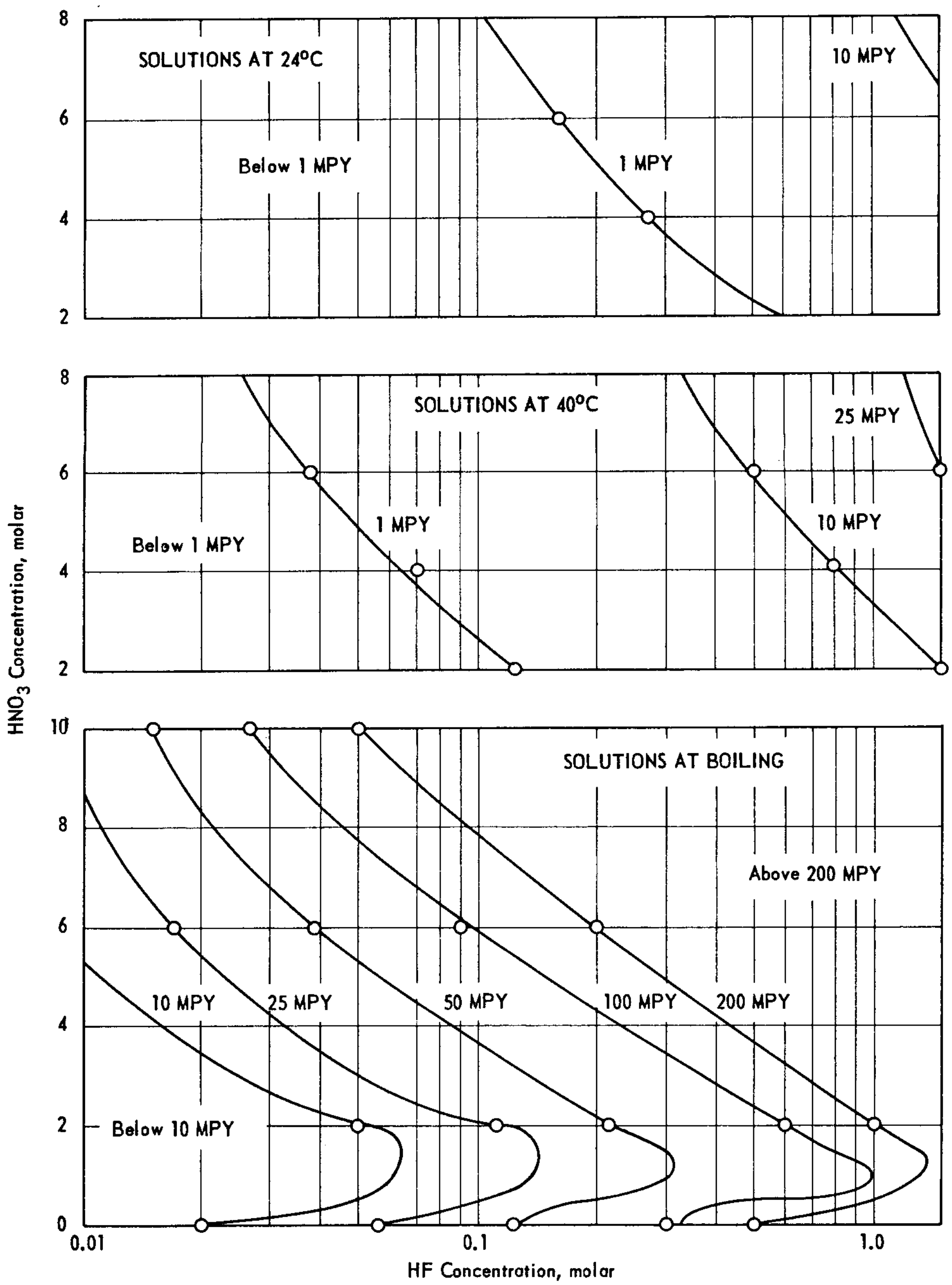


FIG. 3 CORROSION OF 309 SCb IN HNO_3-HF SOLUTIONS

As the HF concentration was increased the allowable HNO_3 concentration had to be decreased to obtain an acceptable corrosion rate.

ADDITIONS OF FUEL ELEMENT MATERIALS

In the dissolution of fuel elements, the stainless steel equipment will only be exposed to straight HNO_3-HF solutions in the initial stages. Therefore, the effect of zirconium, uranium, and molybdenum on the corrosion rate of 309SCb was of interest. In initial experiments the compounds ZrF_4 and $UO_2(NO_3)_2$ were added to simulate conditions during and after the dissolution process. Table V summarizes these data. Since the corrosion data using the compounds were difficult to interpret, experiments were run adding the metals to the HNO_3-HF solutions. Table VI summarizes these data.

Effect of ZrF_4

The addition of ZrF_4 to HNO_3-HF solutions increased the corrosion rate of 309SCb stainless steel. The following table typifies the effect of ZrF_4 additions to HNO_3-HF solutions.

Corrosion Rates of 309SCb Stainless Steel
in boiling HNO_3-HF with ZrF_4 Additions

Solution Composition, M			Corrosion Rate, mpy
HNO_3	HF	ZrF_4	
3.0	0.05	0	15
3.0	0.05	0.01	16
3.0	0.05	0.05	35
3.0	0.05	0.5	45

Additions of ZrF_4 to HNO_3-HF solutions increased the corrosion rate of 309SCb by increasing the fluoride content of the solution. When the corrosion rates of solutions containing 0.25M total fluoride were compared, the fluoride being supplied either by HF alone or by a combination of HF and ZrF_4, it appeared that ZrF_4 complexed about half its formula weight of fluoride.

In mixed acid solutions containing 0.1M $UO_2(NO_3)_2$, increasing ZrF_4 concentration from 0 to 0.5M increased the corrosion rate from 14 to 47 mpy. In 1.5M $UO_2(NO_3)_2$ mixed acid solutions, increasing ZrF_4 from 0 to 0.5M increased the corrosion rate from 5.4 to 54 mpy.

Effect of $UO_2(NO_3)_2$

In 0.05M HF solutions with the HNO_3 concentration below 3.0M, additions of $UO_2(NO_3)_2$ decreased the corrosion rate of 309SCb. In 10M HNO_3 and 0.05M HF solutions, increasing $UO_2(NO_3)_2$ from 0.1 to 0.5M increased the corrosion rate of 309SCb from 165 to 182 mpy.

$UO_2(NO_3)_2$ additions at two ZrF_4 concentrations, 0.01 and 0.5M, in the mixed acid solutions did not alter the corrosion rate significantly. At the lower ZrF_4 concentration, increasing $UO_2(NO_3)_2$ from 0 to 1.5M decreased the corrosion rate from 13 to 7.5 mpy. At the higher ZrF_4 concentration, increasing $UO_2(NO_3)_2$ from 0 to 1.5M increased the corrosion rate from 45 to 58 mpy.

Effect of Zirconium

Dissolving 0.0125M zirconium metal in solutions containing 0.05M HF and varying concentrations of HNO_3 reduced the corrosion rate of 309SCb by a factor of more than two. This reduction in corrosion rate was due to complexing of the fluoride to form a zirconium fluoride. From the corrosion data it appeared that ZrF_2 or ZrF_3 was forming, rather than ZrF_4 as predicted. Therefore, to simulate dissolving conditions for corrosion tests, the use of ZrF_4 was unrealistic. To determine the effects of zirconium in HNO_3-HF solutions the metal should be used, rather than a fluoride salt.

Effect of Uranium

Two concentrations of uranium were studied in 0.05M HF and varying HNO_3 concentration solutions. At the lower concentration of 0.0083M uranium, no significant effect on the corrosion rate was observed. However, dissolving 0.1M uranium metal in the mixed acid solutions reduced the corrosion rate of 309SCb. Uranium evidently complexed the fluoride to some extent, but it was not nearly so effective as zirconium.

Effect of Molybdenum

Addition of 0.0083M molybdenum reduced the corrosion rate of 309SCb stainless steel in mixed acid solutions containing 3.0M or less HNO_3. In the 0.05M HF and 3.0M HNO_3 solution, 0.0083M Mo decreased the corrosion rate of 309SCb from 15 to 12 mpy. Molybdenum probably complexed the fluoride better than uranium, but not so well as zirconium.

EFFECT OF ALUMINUM

As previously noted for 304L, the addition of one mole of $Al(NO_3)_3$ for every three moles of fluoride effectively lowered the corrosion rate of wrought 309SCb, as shown in Table VII.

EFFECT OF REDUCIBLE CATIONS

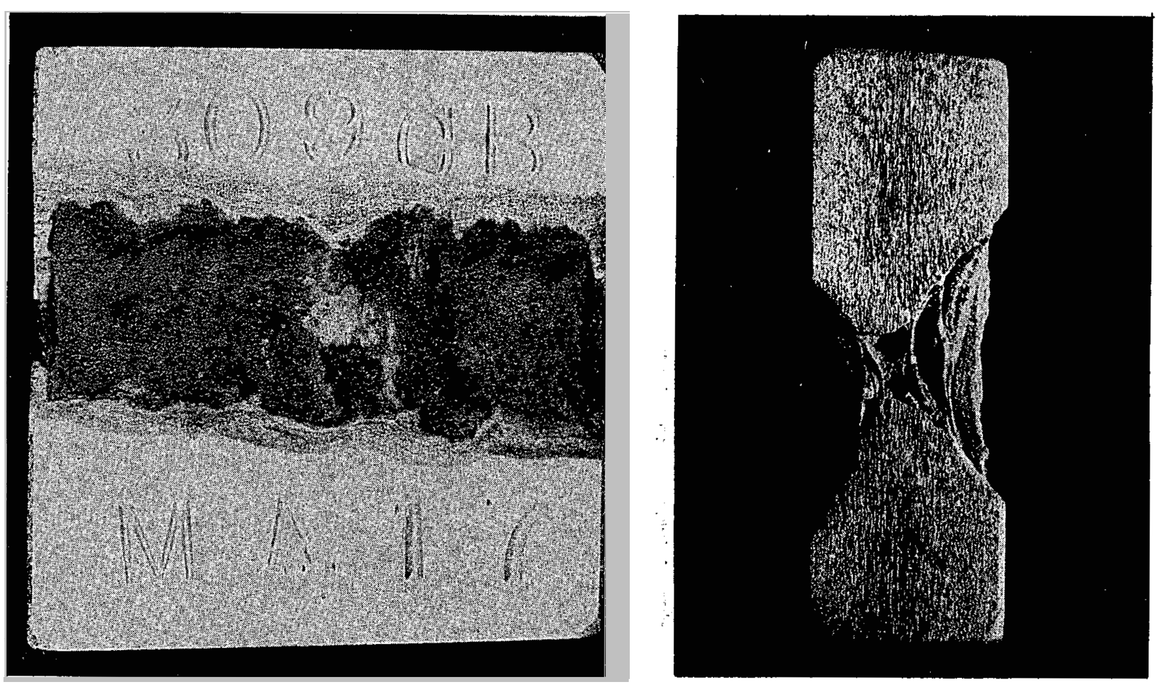
No significant reduction in corrosion rate of 309SCb was obtained by adding 0.02M $AgNO_3$, $Fe(NO_3)_3$, or $Cu(NO_3)_2$ to boiling 3.0M HNO_3 and 0.075M HF solutions.

CORROSION OF 309SCb WELDS

Although the corrosion resistance of wrought 309SCb was adequate for handling boiling HNO_3-HF solutions, welds made with 309SCb filler rod suffered severe preferential corrosion. Table VIII summarizes the corrosion data for welded 309SCb in HNO_3-HF solutions. The corrosion behavior of both metal arc and Heliarc 309SCb welds was evaluated.

METAL ARC WELDS

Metal arc welds corroded at much higher corrosion rates in boiling HNO_3-HF solutions than did wrought 309SCb. **Figure 4 shows a coupon** after 580 hours of test in a boiling 3.0M HNO_3 and 0.075M HF solution. The weld corroded preferentially at a rate of 630 mpy, while the corrosion rate of the base metal was only 25 mpy.



Neg. 20020 **Mag. 3X**

Weld has been severely preferentially attacked while wrought metal has not suffered appreciable attack.

Neg. 20043 **Mag. 3X**

Edge view of corrosion coupon shows how the weld has been preferentially corroded.

FIG. 4 CORROSION OF METAL ARC 309SCb WELDS
(Tested 580 hours in boiling 3.0M HNO_3 – 0.075M HF)

For wrought 309SCb it was shown that concentrations of from 0.05 to 1.0M HNO_3 inhibited corrosion in boiling 0.075M HF solutions. This effect of HNO_3 concentration was also observed for welded 309SCb, as shown in Figure 5. Reducing the HNO_3 concentration to less than 1.0M in boiling 0.075M HF solutions reduced the corrosion rate of the weld to less than 25 mpy. Figure 6 shows the weld zone after 480 hours in test.

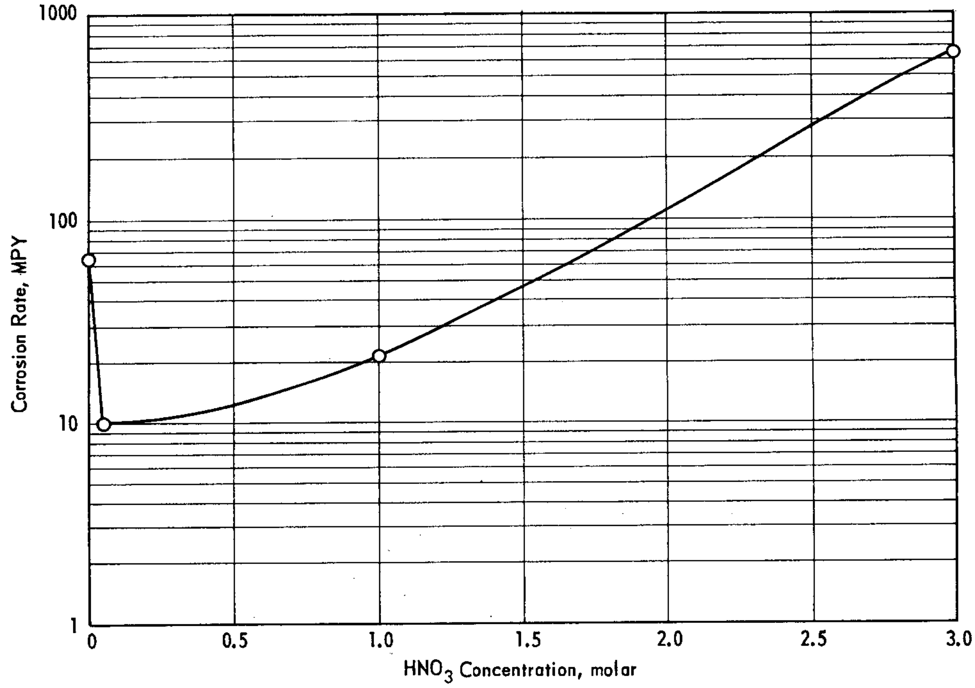
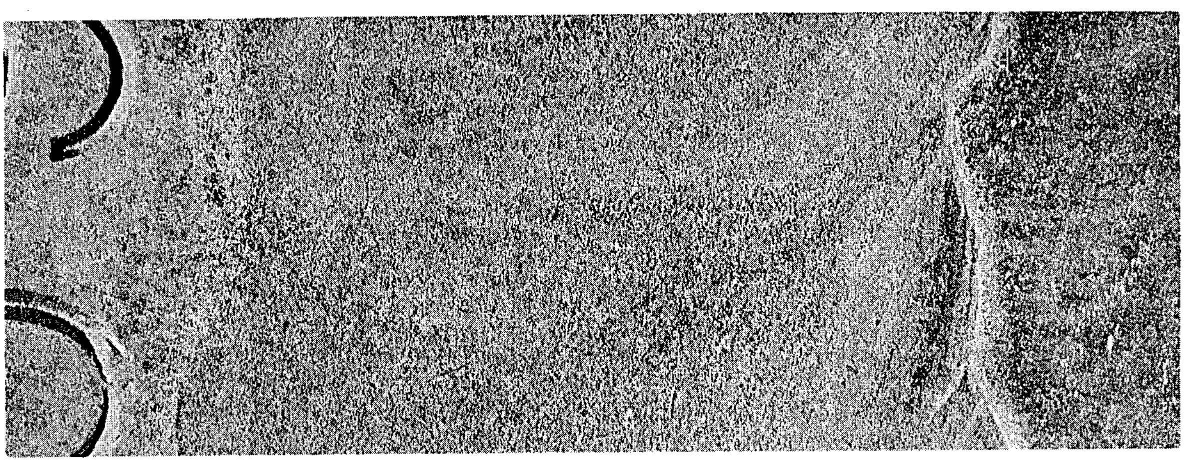


FIG. 5 CORROSION OF 309 SCb WELDS IN BOILING 0.075M HF WITH VARYING HNO_3 CONCENTRATION



Neg. 26672 Mag. 10X

After 480 hours in boiling 1.0M HNO_3 and 0.075M HF, the 309 SCb weld did not corrode preferentially. Figure 4 shows the severe weld corrosion that occurred in 3.0M HNO_3 and 0.075M HF solutions.

FIG. 6 EFFECT OF LOW HNO_3 CONCENTRATION ON WELD CORROSION

Mechanism of Weld Attack in HNO_3-HF

The mechanism of corrosion of 309SCb welds was determined to be chemical attack of the columbium carbide particles that are precipitated in a continuous network at the grain boundaries. The investigation leading to this conclusion was conducted with the electron microscope using X-ray diffraction.

Effect of Aluminum, Zirconium, and Uranium

Since the corrosion rate of 309SCb welds was much higher than that of wrought 309SCb under the same test conditions, a greater concentration of complexing agent was required to reduce the weld corrosion rate to an acceptable level. In boiling 3.0M HNO_3 and 0.075M HF solutions, at least one mole of aluminum per mole of fluoride was required to reduce weld corrosion to 50 mpy as shown in Figure 7.

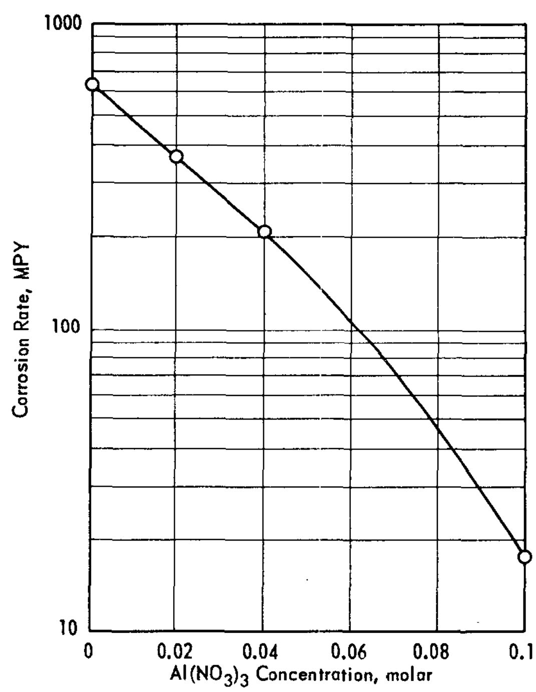


FIG. 7 CORROSION OF 309 SCb WELDS IN BOILING 3.0 M HNO_3 - 0.075M HF SOLUTIONS WITH ADDITIONS OF $Al(NO_3)_3$

Increasing the HF concentration in boiling 3.0M HNO_3 solutions further increased the aluminum-to-fluoride ratio required to lower the weld corrosion rate to 50 mpy. In 3.0M HNO_3 and 0.4M HF solutions, increasing the $Al(NO_3)_3$ concentration from 0.13 to 0.4M reduced the corrosion rate of 309SCb welds from 1330 to 99 mpy and that of wrought 309SCb from 66 to 0.5 mpy. Figure 8a shows the welded coupons tested at these conditions. Probably a ratio of at least 1.25 moles of aluminum per mole of fluoride would be required to reduce the weld corrosion rate to less than 50 mpy in this solution.

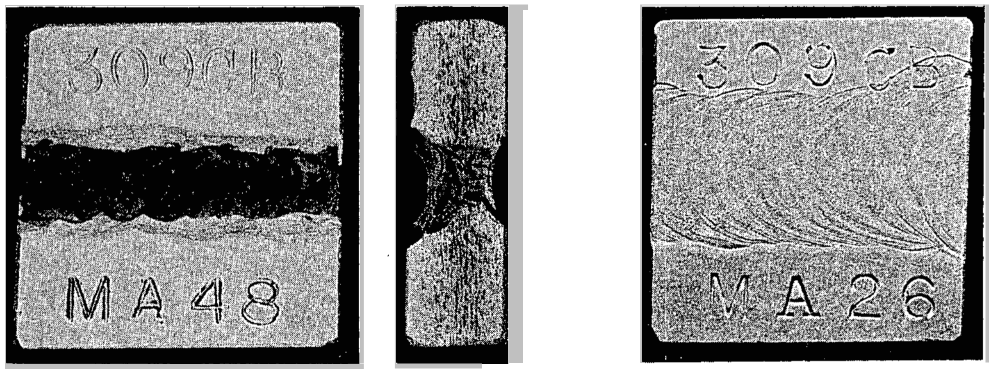
To represent a solution after dissolution of the Zircaloy cladding of a 2 wt % Zr - U alloy fuel element, 0.06M Zr was added to a boiling 3.0M HNO_3 and 0.4M HF solution. Wrought 309SCb corroded at a rate of 53 mpy, while 309SCb welds corroded at a rate above 1000 mpy. Addition of 0.13M $Al(NO_3)_3$ to this solution reduced the corrosion rate of wrought 309SCb to 13 mpy and of 309SCb welds to 390 mpy. Figure 8b shows the welded coupons after test.

After completion of the dissolving cycle, the 3.0M HNO_3 and 0.4M HF solution would contain 0.1M Zr and 0.5M U. The corrosion rate of both wrought and welded 309SCb was below 0.2 mpy in this solution. Increasing the fluoride to 0.475M HF in this solution increased the weld corrosion rate to 13 mpy.

HF Solutions

Boiling HF solutions did not attack the welds selectively. However, a fine pitting attack of wrought and weld metal was observed, and dark grey films characteristic of fluoride corrosion formed on the test coupons.

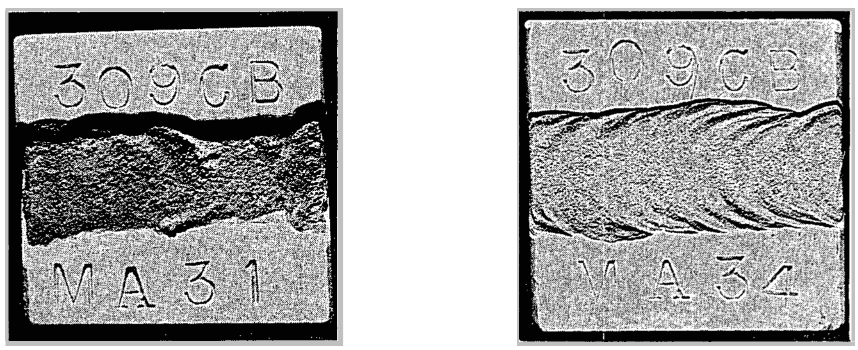
In the absence of HNO_3, the addition of 1 mole of aluminum for every 3 moles of fluoride adequately reduced the corrosion of welded 309SCb. The addition of 0.13M $Al(NO_3)_3$ to a boiling 0.4M HF solution reduced the corrosion rate of welded 309SCb coupons from 225 to 10 mpy. Figure 8c shows the coupons after test.



Neg. 19795 Neg. 19796
With 0.13M $Al(NO_3)_3$, corrosion rate was 1330 mpy.

Neg. 20188
With 0.4M $Al(NO_3)_3$, corrosion rate was lowered to 99 mpy.

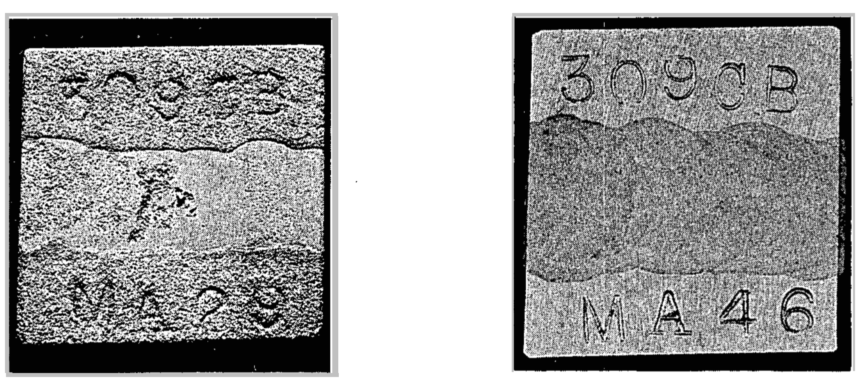
a. Boiling 3.0M HNO_3, 0.4M HF, and $Al(NO_3)_3$



Neg. 20190
Without $Al(NO_3)_3$, corrosion rate was 1070 mpy.

Neg. 20192
With 0.13M $Al(NO_3)_3$, corrosion rate was lowered to 390 mpy.

b. Boiling 3.0M HNO_3, 0.4M HF, and 0.06M Zr



Neg. 20331
Without $Al(NO_3)_3$, corrosion rate was 225 mpy.

Neg. 19794
With 0.13M $Al(NO_3)_3$, or one mole of Al for every three moles of fluoride, corrosion rate was 10 mpy.

c. Boiling 0.4M HF

FIG. 8 EFFECT OF $Al(NO_3)_3$ ON CORROSION OF 309SCb WELDS
(Mag. 1.7X)

A boiling 1.6M HF and 0.375M Zr solution corroded welded 309SCb at a rate of 36 mpy. No severe preferential weld corrosion occurred. However, both the wrought metal and the weld were severely pitted, as shown in Figure 9. Pits up to 9 mils deep were developed in 240 hours. Coupons tested in this solution formed heavy grey films, and this film resulted in the initiation of pitting conditions on the stainless steel surface.

Neg. 20194 Mag. 3 X

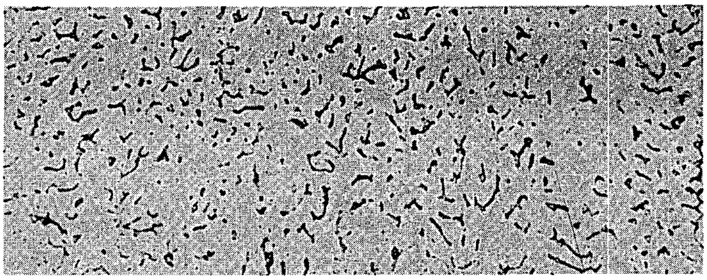
After 240 hours in test in boiling 1.6 M HF and 0.375 M Zr, pits up to 9 mils deep were measured. As noted in previous work, the weld was not preferentially attacked in the HF solution without HNO_3.

FIG. 9 CORROSION OF 309SCb IN A HF – Zr SOLUTION

Effect of Heat Treatment

Heat treatment of metal-arc-welded 309SCb coupons reduced the corrosion rate of the welds. The most important effect of annealing, from a corrosion standpoint, was coalescence of the columbium carbide particles so that a continuous network no longer existed.

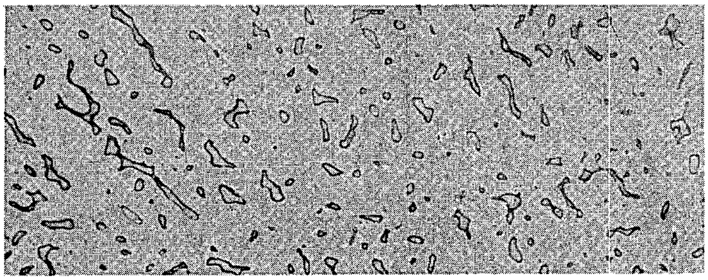
Annealing metal-arc-welded coupons 30 minutes at 1950°F and water quenching reduced the weld corrosion rate from 630 mpy to 50 mpy in boiling 3.0M HNO_3 and 0.075M HF. Increasing the annealing time to 6, 16, and 50 hours did not further improve the weld corrosion resistance. Figure 10 shows the microstructure of the welds heat treated for varying lengths of time.



As-Welded

Second phase dendrites
of ferrite and CbC

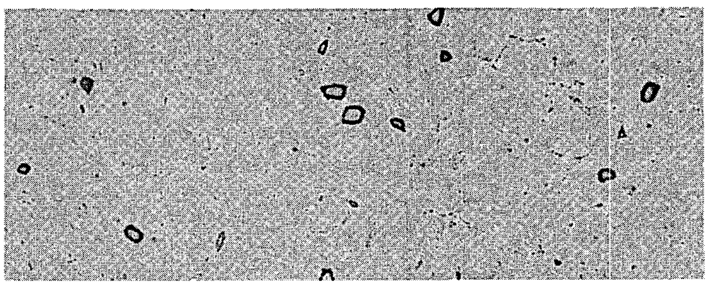
Neg. 20045



Annealed 30 min. at 1950°F, w.q.

Ferrite and CbC were coalesced.

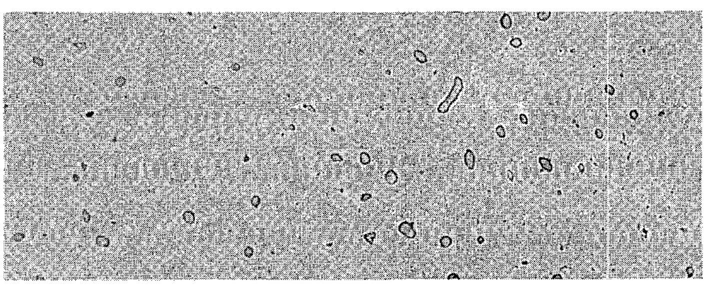
Neg. 20046



Annealed 6 hr. at 1950°F, w.q.

Part of ferrite was transformed
to austenite.

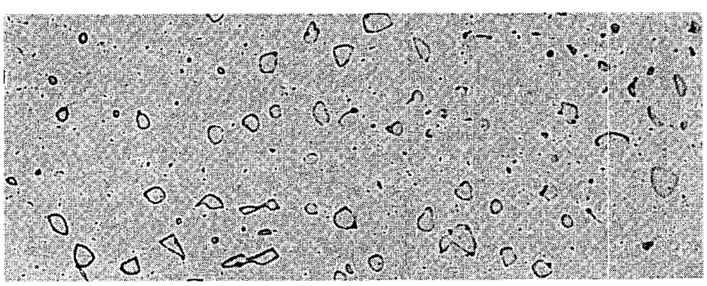
Neg. 19721



Annealed 16 hr at 1950°F, w.q.

CbC was further coalesced.

Neg. 19767



Annealed 50 hr at 1950°F, w.q.

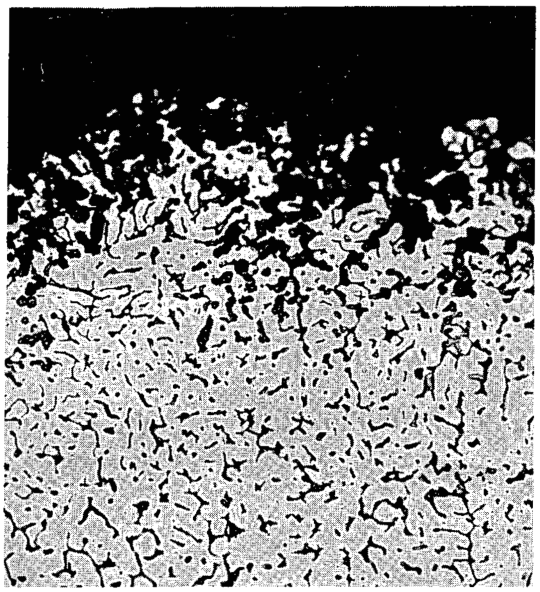
CbC was further coalesced.

Neg. 20382

FIG. 10 MICROSTRUCTURE OF 309 SCb METAL ARC WELDS
(Concentrated Murakami's Etch – Mag. 425X)

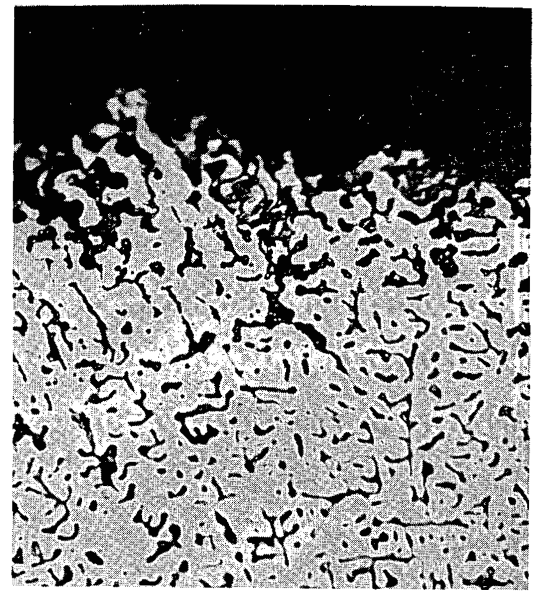
HELIARC WELDS

Although Heliarc 309SCb welds corrode preferentially in HNO_3-HF solutions, the corrosion rate was lower than that observed for metal arc welds. One reason for the slightly better resistance of the Heliarc weld might be the size of the dendrites in the weld microstructure. Figure 11 shows cross sections of two corroded welds. In the metal arc weld the fine dendrites allowed corrosion to proceed at an increasing rate. The Heliarc weld had somewhat coarser dendrites which resulted in a lower corrosion rate.



Neg. 19036 Mag. 250 X

Metal Arc



Neg. 19037 Mag. 250 X

Heliarc

Oxalic Acid Etch

Intergranular corrosion of the Heliarc proceeded at a slower rate than the metal arc weld due to its coarser structure.

FIG. 11 CROSS SECTIONS OF CORRODED 309SCb WELDS
(Tested 240 hours in boiling 3.0M HNO_3 – 0.075 M HF)

Effect of Heat Treatment

Annealing Heliarc-welded 309SCb for 30 minutes at 1950°F and water quenching reduced the weld corrosion rate from 151 to 55 mpy in boiling 3.0M HNO_3 and 0.075M HF solutions. Further annealing for 6 and 16 hours did not significantly decrease the weld corrosion rate. Metallographic examination of the Heliarc 309SCb welds showed that annealing caused the columbium carbides and the ferrite to coalesce. Longer annealing times up to 16 hours transformed part of the ferrite to austenite. In general, the structure of 309SCb metal arc and Heliarc welds were similar.

CORROSION OF 308L WELDS

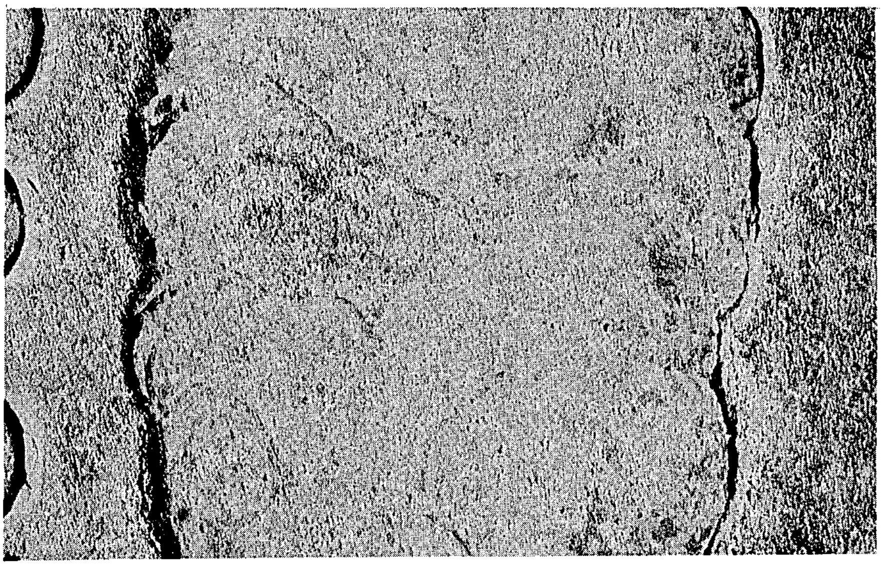
Since 309SCb welds are susceptible to cracking, 309SCb equipment is frequently welded with 308L filler rod to provide a more ductile weld. In boiling HNO_3-HF solutions, the corrosion rate of the 308L weld was equal to that of wrought 309SCb. However, "knifeline" attack occurred in the base metal adjacent to the weld. As reported in Reference 2, this "knifeline" attack was found to be due to chemical attack of the columbium carbides precipitated at the grain boundaries in the heat-affected zone of the base metal. The better corrosion resistance of the 308L weld compared to the 309SCb weld was due to the low carbon content of the weld and the absence of columbium carbide networks within the weld.

The corrosion behavior of both Heliarc and metal arc 308L welds was approximately the same. Corrosion data are presented in the following table.

Corrosion of 309SCb Welded with 308L in Boiling HNO_3-HF Solutions

Weld	Solution Composition, M		Time in Test	Corrosion Rate, mpy
	HNO_3	HF		
Heliarc 308L	14.3	-	240	3.6
Heliarc 308L	-	0.075	288	46
Heliarc 308L	3.0	0.075	480	37
Metal arc 308L	14.3	-	240	3.6
Metal arc 308L	-	0.075	240	37
Metal arc 308L	3.0	0.075	288	36

In boiling 14.3M HNO_3 (Huey Test) no evidence of "knifeline" attack was observed. However, in boiling 3.0M HNO_3 and 0.075M HF "knifeline" attack was observed at the interface between the weld and base metal. Figure 12 shows the metal arc 308L welded coupon after 480 hours in test. The weld was not preferentially corroded. However, the base metal adjacent to the weld corroded 18 mils in 480 hours. Metallographic examination of the "knifeline" crevice showed that intergranular corrosion had occurred.



"Knifeline" attack of 309SCb welded with 308L after 480 hours in boiling 3.0M HNO_3 and 0.075M HF

Neg. 21166

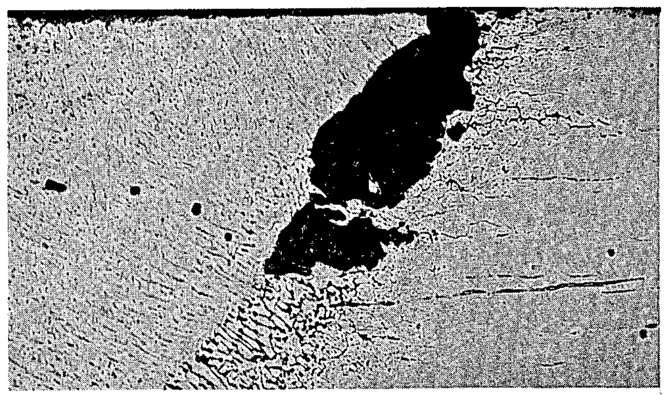
Mag. 10X

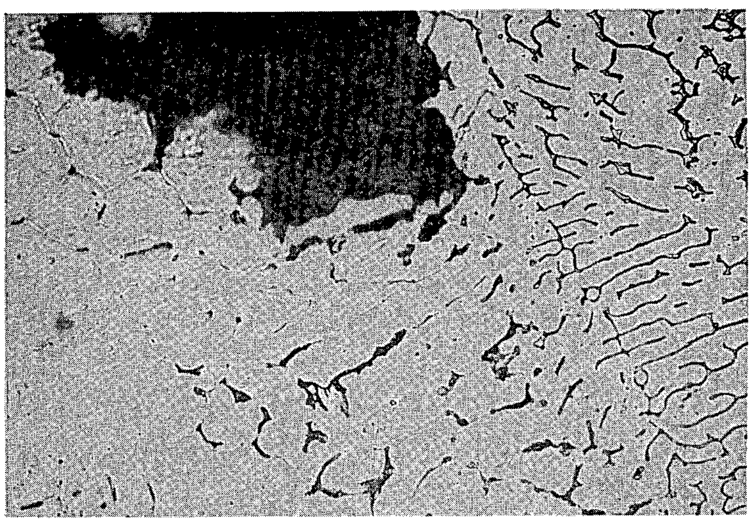
"Knifeline" attack occurred in the base metal adjacent to the weld. In 480 hours the attack had penetrated 18 mils.

Chromic acid etch

Neg. 26778

Mag. 100X





"Knifeline" attack was due to intergranular corrosion caused by chemical attack of the columbium carbides precipitated in the base metal adjacent to the weld.

Oxalic acid etch

Neg. 21169

Mag. 500X

FIG. 12 "KNIFELINE" ATTACK

The "knifeline" corrosion of wrought 309SCb base metal undoubtedly also occurs when the weld is made with 309SCb filler metal. But, in this case, the corrosion resistance of the 309SCb filler metal is so poor that the "knifeline" effect is obscured.

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2. Angerman, C. L. and P. M. Kranzlein. "Mechanism of Corrosion of Stabilized Stainless Steel". Paper presented at Metallurgical Engineering Colloquium. Univ. of Notre Dame, April 28, 1960.

TABLE I

SUMMARY OF HNO_3-HF CORROSION DATA

(304L Stainless Steel)

Solution Composition, M HNO_3	Solution Composition, M HF	Temp, °C	Corrosion Rate, mpy
0.05	0.05	60	32
0.1	2.7	24	701
1.0	0.05	60	17
2.0	0.1	24	7.7
2.0	0.5	24	93
2.0	1.0	24	160
2.0	1.5	24	211
2.0	0.01	40	1.4
2.0	0.025	40	6.3
2.0	0.05	40	15
2.0	0.075	40	22
2.0	0.1	40	34
2.0	0.5	40	187
2.0	1.0	40	386
2.0	1.5	40	506
2.0	0.01	60	3.4
2.0	0.025	60	18
2.0	0.05	60	28
2.0	0.075	60	47
2.0	0.1	60	71
2.0	0.5	60	364
2.0	1.0	60	748
2.0	1.5	60	1100
2.0	0.05	Boiling	92
2.0	0.1	Boiling	187
2.0	0.5	Boiling	1093
2.0	1.0	Boiling	1214
2.5	1.5	60	710
3.0	0.03	60	8.9
3.0	0.05	60	19
3.0	0.075	60	35
3.0	0.075	60	26 (a)
3.0	0.075	Boiling	177 (a)
3.2	0.02	Boiling	19
4.0	0.01	24	0.28
4.0	0.025	24	0.65
4.0	0.05	24	1.7
4.0	0.075	24	3.8
4.0	0.1	24	5.4
4.0	0.5	24	59
4.0	1.0	24	120
4.0	1.5	24	193
4.0	0.01	40	0.52
4.0	0.025	40	1.1
4.0	0.05	40	3.4
4.0	0.075	40	8.2
4.0	0.1	40	19
4.0	0.5	40	134
4.0	1.0	40	296
4.0	1.5	40	397

Solution Composition, M HNO_3	Solution Composition, M HF	Temp, °C	Corrosion Rate, mpy
4.0	0.05	Boiling	134
4.0	0.1	Boiling	301
4.0	0.5	Boiling	987
4.0	1.0	Boiling	1545
5.0	0.04	Boiling	78
5.0	2.0	60	875
6.0	0.01	24	0.22
6.0	0.025	24	0.64
6.0	0.05	24	1.2
6.0	0.075	24	1.9
6.0	0.1	24	3.5
6.0	0.5	24	36
6.0	1.0	24	83
6.0	1.5	24	130
6.0	0.01	40	0.70
6.0	0.025	40	2.3
6.0	0.05	40	5.5
6.0	0.075	40	8.5
6.0	0.1	40	14
6.0	0.5	40	113
6.0	1.0	40	265
6.0	1.5	40	372
6.0	0.01	60	2.6
6.0	0.025	60	6.9
6.0	0.05	60	18
6.0	0.075	60	33
6.0	0.1	60	44
6.0	0.5	60	300
6.0	1.0	60	705
6.0	1.5	60	850
6.0	0.05	Boiling	180
6.0	0.1	Boiling	434
6.0	0.5	Boiling	1555
6.0	1.0	Boiling	2497
6.8	0.06	Boiling	112
10.0	0.01	60	3.8
10.0	0.025	60	12
10.0	0.05	60	27
10.0	0.075	60	37
10.0	0.1	60	52
10.0	0.5	60	197
10.0	1.0	60	458
10.0	1.5	60	563
12.0	0.1	60	73

(a) Samples welded with 308L filler rod.

TABLE II

CORROSION OF 304L IN HNO_3-HF SOLUTIONS CONTAINING Zr AND U AT 60°C

Solution Composition, M					Corrosion Rate, mpy		
HNO_3	HF	ZrF_4	$UO_2(NO_3)_2$	Mo	Vapor	Interface	Liquid
0.05	0.05				0.2	11	32
1.0	0.05				0.1	6.5	17
3.0	0.05				0.4	5.2	19
10.0	0.05				8.0	25	28
0.05	0.05	0.01	0.1		0.2	0.1	0.2
1.0	0.05	0.01	0.1		0.1	0.6	1.9
3.0	0.05	0.01	0.1		0.2	3.0	6.9
10.0	0.05	0.01	0.1		6.1	20	25
3.0	0.03	0.005			0.3	3.2	16
3.0	0.03	-			0.3	3.3	8.9
3.0	0.04	0.0025			0.3	4.7	14
0.05	0.05	0.05	0.15		0.1	0.2	0.1
1.0	0.05	0.05	0.15		0.5	2.5	2.7
3.0	0.05	0.05	0.15		0.5	6.1	6.8
10.0	0.05	0.05	0.15		9.4	25	25
0.05	0.05	0.5	1.5		0.0	0.4	0.5
1.0	0.05	0.5	1.5		0.1	1.6	2.1
3.0	0.05	0.5	1.5		0.5	6.1	6.6
10.0	0.05	0.5	1.5		6.9	18	22
3.0	0.02	0.00855	0.0001	0.0175	0.5	2.4	3.8
Above solution with 0.01M $Al(NO_3)_3$					0.2	1.1	1.2

TABLE III

SUMMARY OF HNO_3-HF-Al CORROSION DATA

(304L Stainless Steel)

Solution Composition, M			Temp,	Corrosion
HNO_3	HF	$Al(NO_3)_3$	°C	Rate, mpy
0.1	2.7	0.1	24	252
0.1	2.7	0.5	24	93
0.1	2.7	0.75	24	28
0.1	2.7	1.0	24	3.7
1.65	1.25	2.5	24	0.2
2.0	0.5	0.1	24	36
2.0	0.5	0.25	24	4.9
2.0	0.5	0.5	24	0.12
2.0	0.5	0.25	40	15
2.0	0.5	0.5	40	0.5
2.0	1.0	0.1	24	134
2.0	1.0	0.25	24	44
2.0	1.0	0.5	24	2.6
2.0	1.0			
2.0	1.0			
2.0	1.5	0.1	24	170
2.0	1.5	0.25	24	81
2.0	1.5	0.5	24	17
2.0	1.5	0.75	24	0.8
2.0	1.5	1.5	24	0.2
2.0	1.5	0.25	40	285
2.0	1.5	0.5	40	52
4.0	0.5	0.1	24	15
4.0	0.5	0.125	24	11
4.0	0.5	0.25	24	1.9
4.0	0.5	0.5	24	0.2

Solution Composition, M			Temp,	Corrosion
HNO_3	HF	$Al(NO_3)_3$	°C	Rate, mpy
4.0	1.0	0.1	24	51
4.0	1.0	0.25	24	38
4.0	1.0	0.5	24	1.7
4.0	1.0	0.75	24	0.5
4.0	1.0	1.0	24	0.4
4.0	1.5	0.1	24	95
4.0	1.5	0.25	24	95
4.0	1.5	0.5	24	9.0
4.0	1.5	0.75	24	1.3
4.0	1.5	1.5	24	0.4
6.0	0.5	0.1	24	17
6.0	0.5	0.25	24	2.2
6.0	0.5	0.125	40	42
6.0	0.5	0.25	40	7.0
6.0	0.5	0.5	40	1.2
6.0	1.0	0.1	24	39
6.0	1.0	0.25	24	31
6.0	1.0	0.5	24	2.5
6.0	1.0	0.5	40	9.0
6.0	1.0	1.0	40	3.9
6.0	1.5	0.1	24	88
6.0	1.5	0.25	24	71
6.0	1.5	0.5	24	3.6
6.0	1.5	0.5	40	12
6.0	1.5	0.75	40	11
6.0	1.5	1.5	40	4.9

TABLE IV

SUMMARY OF HNO_3-HF CORROSION DATA

(309SCb Stainless Steel)

Solution Composition, M: HNO_3	Solution Composition, M: HF	Temp, °C	Corrosion Rate, mpy
0	0.075	Boiling	33
0	0.2	Boiling	85
0	0.4	Boiling	215
0.05	0.05	Boiling	3.1
0.05	0.25	Boiling	81
0.05	1.0	Boiling	259
0.1	2.7	24	318
1.0	0.05	Boiling	5.1
1.0	0.25	Boiling	38
1.0	1.00	Boiling	92
2.0	0.1	24	0.13
2.0	0.5	24	1.1
2.0	1.0	24	2.7
2.0	1.5	24	4.9
2.0	0.01	40	0.02
2.0	0.025	40	0.18
2.0	0.05	40	0.76
2.0	0.075	40	0.70
2.0	0.1	40	0.95
2.0	0.5	40	3.4
2.0	1.0	40	7.6
2.0	1.5	40	12
2.0	0.01	60	0.35
2.0	0.025	60	0.66
2.0	0.05	60	0.9
2.0	0.075	60	1.9
2.0	0.1	60	2.2
2.0	0.5	60	12
2.0	1.0	60	32
2.0	1.5	60	53
2.0	0.05	Boiling	10
2.0	0.1	Boiling	26
2.0	0.5	Boiling	125
2.0	1.0	Boiling	253
2.5	1.5	60	44
3.0	0.05	Boiling	15
3.0	0.25	Boiling	63
3.0	1.0	Boiling	339
4.0	0.1	24	0.03
4.0	0.025	24	0.09
4.0	0.05	24	0.13
4.0	0.075	24	0.20
4.0	0.1	24	0.28
4.0	0.5	24	1.7
4.0	1.0	24	3.5
4.0	1.5	24	5.0
4.0	0.01	40	0.18
4.0	0.025	40	0.30
4.0	0.05	40	0.57
4.0	0.075	40	0.90
4.0	0.1	40	1.3
4.0	0.5	40	6.4
4.0	1.0	40	12
4.0	1.5	40	18
4.0	0.05	Boiling	25
4.0	0.1	Boiling	52
4.0	0.5	Boiling	274
4.0	1.0	Boiling	510
5.0	2.0	60	164
6.0	0.01	24	0.07
6.0	0.025	24	0.24
6.0	0.05	24	0.39
6.0	0.075	24	0.49
6.0	0.1	24	0.77
6.0	0.5	24	3.0
6.0	1.0	24	5.6
6.0	1.5	24	9.0
6.0	0.01	40	0.42
6.0	0.025	40	0.78
6.0	0.05	40	1.3
6.0	0.075	40	1.8
6.0	0.1	40	2.3
6.0	0.5	40	10
6.0	1.0	40	18
6.0	1.5	40	26
6.0	0.01	60	1.1
6.0	0.025	60	3.4
6.0	0.05	60	5.3
6.0	0.075	60	6.7
6.0	0.1	60	10
6.0	0.5	60	52
6.0	1.0	60	145
6.0	1.5	60	195
6.0	4.0	70	665
6.0	0.05	Boiling	62
6.0	0.1	Boiling	118
6.0	0.5	Boiling	417
6.0	1.0	Boiling	686
8.0	0.01	Boiling	20
10	0.01	60	2
10	0.025	60	10
10	0.05	60	26
10	0.075	60	39
10	0.1	60	48
10	0.5	60	145
10	1.0	60	293
10	1.5	60	355
10	0.025	Boiling	96
10	0.05	Boiling	204
10	0.075	Boiling	367
10	0.25	Boiling	506
10	1.0	Boiling	1115
12	0.01	62	99

TABLE V

CORROSION OF 309SCb IN BOILING HNO_3-HF SOLUTIONS WITH ADDITIONS OF ZrF_4 AND $UO_2(NO_3)_2$

Solution Composition, M				Corrosion Rate, mpy		
HNO_3	HF	ZrF_4	$UO_2(NO_3)_2$	Vapor	Interface	Liquid
3.0	0.03	0.005	-	7.3	9.9	10
3.0	0.03	-	-	2.8	2.7	2.9
3.0	0.04	0.0025	-	9.6	11	11
0.05	0.05	0.01	0.1	1.3	0.8	0.6
1.0	0.05	0.01	0.1	1.9	3.0	2.9
3.0	0.05	0.01	0.1	6.4	8.4	7.9
10.0	0.05	0.01	0.1	159	197	203
0.05	0.05	0.05	0.15	0.3	0.4	0.5
1.0	0.05	0.05	0.15	3.1	3.8	3.6
3.0	0.05	0.05	0.15	11	18	17
10.0	0.05	0.05	0.15	133	241	289
0.05	0.05	0.5	1.5	1.5	4.1	3.7
1.0	0.05	0.5	1.5	3.7	14	11
3.0	0.05	0.5	1.5	14	45	55
10.0	0.05	0.5	1.5	175	185	165
0.05	0.05	0.05				3.0
1.0	0.05	0.05				10
3.0	0.05	0.05				35
10.0	0.05	0.05				267
0.05	0.05	-	0.1			0.4
1.0	0.05	-	0.1			2.7
3.0	0.05	-	0.1			17
10.0	0.05	-	0.1			165
0.05	0.05	-	0.5			0.2
1.0	0.05	-	0.5			3.0
3.0	0.05	-	0.5			12
10.0	0.05	-	0.5			182
3.0	0.05	0.01	-			16
3.0	0.05	0.01	0.1			13
3.0	0.05	0.01	0.15			13
3.0	0.05	0.01	1.5			7.6
3.0	0.05	0.5	-			45
3.0	0.05	0.5	0.1			49
3.0	0.05	0.5	0.15			50
3.0	0.05	0.5	1.5			58
3.0	0.05	-	0.1			14
3.0	0.05	0.01	0.1			13
3.0	0.05	0.05	0.1			18
3.0	0.05	0.5	0.1			49
3.0	0.05	-	1.5			5.4
3.0	0.05	0.01	1.5			7.6
3.0	0.05	0.05	1.5			15
3.0	0.05	0.5	1.5			58

TABLE VI

CORROSION OF 309SCb IN BOILING HNO_3-HF WITH ADDITIONS OF Zr, U, AND Mo

Solution Composition, M					Corrosion Rate, mpy
HNO_3	HF	Zr	U	Mo	
0.05	0.05	0.0125	-	-	0.6
1.0	0.05	0.0125	-	-	1.3
3.0	0.05	0.0125	-	-	7.7
10.0	0.05	0.0125	-	-	65
0.05	0.05		0.0083	-	5.1
1.0	0.05		0.0083	-	7.8
3.0	0.05		0.0083	-	19
10.0	0.05		0.0083	-	179
0.216	0.05	-	0.1	-	0.1
1.0	0.05	-	0.1	-	0.6
3.0	0.05	-	0.1	-	9.0
10.0	0.05	-	0.1	-	135
0.05	0.05	-	-	0.0083	0.9
1.0	0.05	-	-	0.0083	3.5
3.0	0.05	-	-	0.0083	12
10.0	0.05	-	-	0.0083	156

TABLE VII

SUMMARY OF HNO_3-HF-Al CORROSION DATA

(309SCb Stainless Steel)

Solution Composition, M			Temp, °C	Corrosion Rate, mpy
HNO_3	HF	$Al(NO_3)_3$		
0.1	2.7	0.1	24	60
0.1	2.7	0.5	24	1.7
0.1	2.7	0.75	24	1.0
0.1	2.7	1.0	24	0.2
1.65	1.25	2.5	24	0.05
2.0	1.5	0.75	24	0.3
2.0	1.5	1.5	24	0.06
4.0	0.5	0.125	24	0.8
4.0	1.0	0.5	24	0.3
4.0	1.5	0.5	24	1.3
4.0	1.5	0.75	24	0.4
6.0	0.5	0.125	40	4.8
6.0	1.0	0.5	40	4.1
6.0	1.0	0.75	40	5.0
6.0	1.5	0.5	40	6.0
6.0	1.5	0.75	40	5.0

TABLE VIII

CORROSION OF 309SCb WELDED WITH 309SCb IN BOILING HNO_3-HF SOLUTIONS

Weld Description	Heat Treatment	Solution Composition, M: HNO_3	HF	Zr	U	$Al(NO_3)_3$	Corrosion Rate, mpy: Coupon	Weld
-	Wrought	-	0.075	-	-	-	33	-
Metal arc	As-welded	-	0.075	-	-	-	43	63
-	Wrought	0.05	0.075	-	-	-	9.1	-
Metal arc	As-welded	0.05	0.075	-	-	-	10	12
-	Wrought	0.5	0.075	-	-	-	9.9	-
-	Wrought	1.0	0.075	-	-	-	11.0	-
Metal arc	As-welded	1.0	0.075	-	-	-	14	21
-	Wrought	3.0	0.075	-	-	-	25	-
Metal arc	As-welded	3.0	0.075	-	-	-	226	628
Metal arc	1950°F, 30 min w.q.[a]	3.0	0.075	-	-	-	33	49
Metal arc	1950°F, 6 hr w.q.[a]	3.0	0.075	-	-	-	28	34
Metal arc	1950°F, 16 hr w.q.[a]	3.0	0.075	-	-	-	33	49
Metal arc	1950°F, 50 hr w.q.[a]	3.0	0.075	-	-	-	50	100
Metal arc	1650°F, 2 hr w.q.[a]	3.0	0.075	-	-	-	190	613
Metal arc	1650°F, 20 hr w.q.[a]	3.0	0.075	-	-	-	135	354
Heliarc	As-welded	3.0	0.075	-	-	-	67	151
Heliarc	1950°F, 30 min w.q.[a]	3.0	0.075	-	-	-	35	55
Heliarc	1950°F, 6 hr w.q.[a]	3.0	0.075	-	-	-	32	46
Heliarc	1950°F, 16 hr w.q.[a]	3.0	0.075	-	-	-	51	103
Metal arc	As-welded	3.0	0.075	-	-	0.02	133	370
Metal arc	As-welded	3.0	0.075	-	-	0.04	75	215
Metal arc	As-welded	3.0	0.075	-	-	0.1	6.8	18
-	Wrought	-	0.2	-	-	-	85	-
-	Wrought	3.0	0.2	0.05	0.25	-	3.8	-
Metal arc	As-welded	3.0	0.2	0.05	0.25	-	4.3	-
-	Wrought	3.0	0.2	0.05	0.25	0.066	0.5	-
Metal arc	As-welded	3.0	0.2	0.05	0.25	0.066	0.3	-
-	Wrought	-	0.4	-	-	-	215	-
Metal arc	As-welded	-	0.4	-	-	-	225	-
Metal arc	Wrought	-	0.4	-	-	0.13	8.1	-
Metal arc	As-welded	-	0.4	-	-	0.13	10	-
-	Wrought	3.0	0.4	0.06	-	-	53	-
Metal arc	As-welded	3.0	0.4	0.06	-	-	392	1070
-	Wrought	3.0	0.4	0.06	-	0.13	13	-
Metal arc	As-welded	3.0	0.4	0.06	-	0.13	139	390
-	Wrought	3.0	0.4	-	-	0.13	66	-
Metal arc	As-welded	3.0	0.4	-	-	0.13	487	1330
-	Wrought	3.0	0.4	-	-	0.4	0.5	-
Metal arc	As-welded	3.0	0.4	-	-	0.4	33	99
-	Wrought	3.0	0.4	0.1	0.5	-	0.2	-
Metal arc	As-welded	3.0	0.4	0.1	0.5	-	0.2	-
-	Wrought	3.0	0.4	0.1	0.5	0.13	0.1	-
Metal arc	As-welded	3.0	0.4	0.1	0.5	0.13	0.1	-
-	Wrought	3.0	0.475	0.1	0.5	-	0.7	-
Metal arc	As-welded	3.0	0.475	0.1	0.5	-	4.7	13
-	Wrought	-	1.6	0.375	-	-	36	-
Metal arc	As-welded	-	1.6	0.375	-	-	34	-

(a) Water quench