Report No. BMI-1571

UC-25 Metals, Ceramics, and
Materials
(TID-4500, 17th Ed.)

Contract No. W-7405-eng-92

ZIRCALOY-4 CORROSION IN HALIDE SOLUTIONS AND AT CREVICES IN HIGH-TEMPERATURE WATER

by

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March 19, 1962

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Some slight localized corrosion was observed in 0 to 0.004–in. crevice assemblies of Zircaloy-4 to Zircaloy-4 to Inconel exposed 84 days to 750 F 1500–psi steam or 680 F water adjusted to pH 10.5 with LiOH or NH_4OH. No accelerated corrosion was observed after 56 days' exposure to 680 F pH 10.5 to 0.01 M solutions of LiCl, LiI, NH_4Cl, or NH_4I with or without Fe_3O_4 suspensions in the solutions. Severe attack occurred in Fe_3O_4–free 680 F 0.01 M LiF and NH_4F solutions. Although large quantities of Fe_3O_4 in suspension decreased attack by decreasing the fluoride concentration of the solution, thin surface deposits of Fe_3O_4 on the Zircaloy-4 surface did not appear to increase or retard attack in the 0.01 M fluoride solutions. No unusual corrosion occurred in 680 F 0.001 M LiF or 0.0001 M NH_4F solutions.

INTRODUCTION

The composition of Zircaloy-2 has recently been modified to minimize hydrogen absorption in the zirconium alloy during corrosion in high-temperature water. The new alloy has been designated Zircaloy-4 and differs from Zircaloy-2 in that it contains no nickel addition and has a somewhat higher iron content. (Zircaloy-4 nominal composition: 1.5 w/o tin, 0.20 w/o iron, 0.10 w/o chromium, 0.007 w/o (max) nickel; Zircaloy-2 nominal composition: 1.5 w/o tin, 0.12 w/o iron, 0.10 w/o chromium, 0.05 w/o nickel).

Although Zircaloy-4 does not differe greatly in composition from Zircaloy-2, there exists the possibility of a difference in corrosion behavior in the primary coolant of pressurized-water reactors. Of particular interest is its corrosion behavior in crevices and under conditions of accidental buildup of halides. The principal halide contaminants might be fluorides (from pickling solutions) and chlorides (from accidental introduction of chloride-contaminated water) although small quantities of iodides also are found in the primary water.

Accordingly, Battelle has undertaken a program for Knolls Atomic Power Laboratory* to study the high-temperature-water corrosion behavior of Zircaloy-4 (1) in crevices in contact with itself and with Inconel Alloy 600** (a nickel-chromium alloy for structural applications) and (2) in fluoride-, chloride-, or iodide-contaminated waters where crud deposits (Fe_3O_4 corrosion products) may contribute to the corrosion attack.

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*Operated by the General Electric Company for the Atomic Energy Commission.

**Trademark of The International Nickel Company, Inc. Inconel Alloy 600 was formerly called Inconel.

EXPERIMENTAL WORK

Procedures

Materials

Knolls Atomic Power Laboratory supplied all the Zircaloy-4, Zircaloy-2, and Inconel specimens and Inconel nuts, bolts, and wires used in the program. Analyses of these materials are given in Table 1. The Zircaloy-4 specimens were all cut from the product of the same ingot.

TABLE 1. ALLOY COMPOSITIONS

		Average Composition[a], w/o									
Alloy	Heat	C	Fe	Ni	Cr	Sn	Ti	Al	N	H	Other
Zircaloy-2 (reference coupons)	HZC-1027	0.009	0.119	0.052	0.097	1.51	<0.001	0.0034	0.0045	0.0012	Bal Zr
Zircaloy-4	HZC-734	0.011	0.199	<0.005	0.089	1.46	<0.002	<0.0031	<0.0029	0.0012	Bal Zr
Inconel	NX7302[b]	0.04	7.20	Bal.	15.85	--	--	--	--	--	0.007 S 0.2 Mn 0.2 Si 0.1 Cu <0.2 Co

(a) Analyses of Zircaloy-2 and Zircaloy-4 supplied by KAPL.
(b) Nominal composition.

Specimen Preparation

Nominal dimensions of Zircaloy specimens for the halide contamination studies were 2.0 by 0.87 by 0.055 in. Dimensions of crevice specimens were 2.5 by 0.49 by 0.095 in. Dimensions of reference specimens in the crevice tests were: Zircaloy-4 – 1.2 by 0.49 by 0.095 in.; Zircaloy-2 – 1.5 by 1.0 by 0.050 in.; and Inconel – 2.0 by 0.87 by 0.058 in. Zircaloy-2 spacers for the crevice specimens measured 0.49 by 0.49 by 0.004 in.

The Zircaloy-4 specimens for the halide tests were precoated at KAPL by pickling 2 mils of surface and then exposing 3 days to neutral degassed 680 F water. Zircaloy-2 and the remaining Zircaloy-4 specimens were pickled at Battelle prior to exposure. Two mils of metal was removed from each surface using an intermittent dip at 120 cycles per min in a 39 volume per cent HNO_3-3.9 volume per cent HF bath at 120 F. The Zircaloy-2 shims used in the crevice specimens were flash-pickled in the above solution to brighten the surface.

Inconel specimens were pickled 15 min in a 21.5 volume per cent HNO_3-5.5 volume per cent HF bath at 125 F. Inconel nuts, bolts, and wires were flash-pickled in the above solution.

In all pickling operations, specimens were transferred immediately from the pickling bath to cold running tap water. After 1 hr in the tap water, the specimens then were rinsed in deionized water, dipped in acetone, and dried.

Exposure Conditions

All the corrosion studies were conducted in 1-liter AISI Type 316 stainless steel autoclaves. Solutions were prepared with deionized water having a specific resistivity greater than 1 megohm-cm.

Halide Corrosion. Corrosion studies were conducted at 680 F in 0.01 M fluoride, chloride, and iodide solutions adjusted to pH 10.5 with LiOH or NH_4OH (six conditions). Reference tests were conducted in pH 10.5 LiOH and NH_4OH solutions with no halides added. Each of the above conditions was also studied with simulated crud (cp Fe_3O_4) added to each autoclave in the ratio of 100 g of crud per liter of solution. A total of 16 conditions were studied in this program.

Stock solutions of the halides were prepared by neutralizing (the LiOH solutions had been passed through a lithium form ion-exchange resin to remove Li_2CO_3) 0.01 M HF, HCl, or HI with LiOH or NH_4OH. Argon was then continuously bubbled through the stock solutions to remove oxygen and maintain it at low levels. The method for final adjustment of pH and introduction of the solution into the autoclaves is shown schematically in Figure 1. The equipment contacting the solutions was made of glass, stainless steel, Teflon, polyethylene, or neoprene rubber. After the system was flushed with argon the halide solution was introduced into a graduated glass vessel where the pH was adjusted to 10.5 with LiOH or NH_4OH. The LiOH was added as a solution, whereas, NH_3 gas was bubbled through the solution to obtain NH_4OH. The required amount of solution was then introduced into a sealed evacuated autoclave which contained the corrosion specimens. The autoclave had been flushed with argon and evacuated a minimum of three times prior to filling with the solution.

One as-pickled and three precoated Zircaloy-4 specimens were exposed to each crud-free condition, while three precoated specimens were exposed to each crudded condition. (The Fe_3O_4 crud was added dry to the autoclaves prior to sealing.) The crud-free autoclaves were opened and the specimens were weighed after total exposures of 3, 14, 28, and 56 days. The crudded autoclaves were opened and the specimens were observed after total exposures of 14, 28, and 56 days. Fresh solutions were added at each exposure period.

Crevice Corrosion. The crevice-corrosion studies were conducted in 680 F degassed water adjusted to pH 10.5 with LiOH or NH_4OH and in 750 F 1500-psi steam. Solution transfer and pH adjustment were done as shown in Figure 1 and as described in the previous section. Two steam tests were used. In one test, the autoclave was half filled with pH 10.5 NH_4OH solution and was run for 6 hr at 680 F. The water was then flashed to steam, the pressure was reduced to 1500 psi, and the temperature was raised to 750 F. In the second steam test, approximately 100 ml of neutral high-purity water was sealed in the autoclave. The autoclave was alternately flushed with argon and then evacuated a minimum of three times. The autoclave finally was heated to 750 F with occasional bleeding of the excess steam to keep the pressure from exceeding 1500 psi.

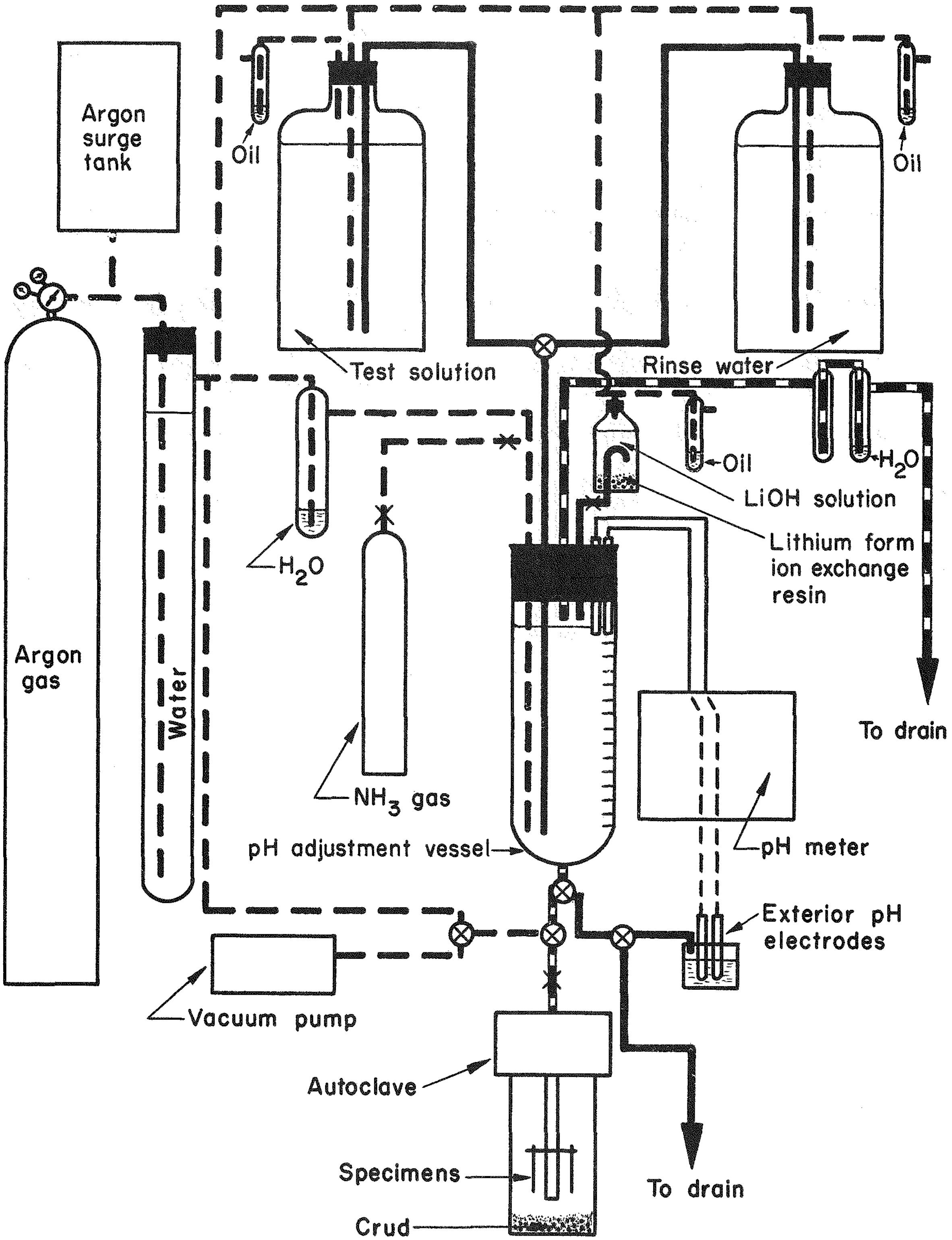
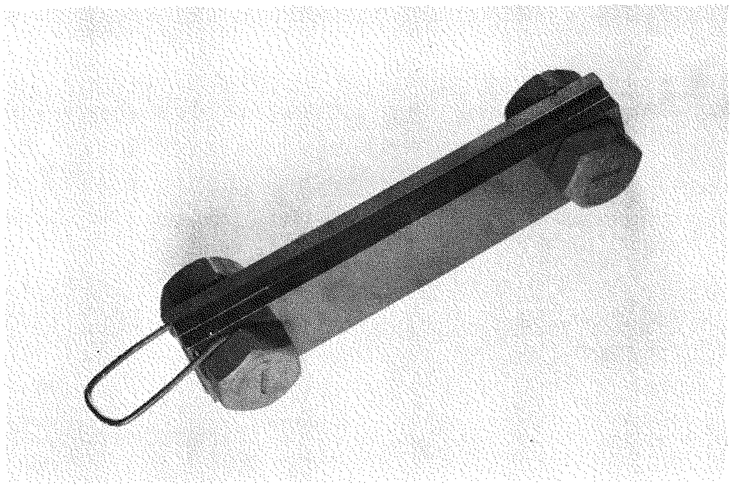


FIGURE 1. SCHEMATIC DIAGRAM OF APPARATUS FOR ADJUSTING pH AND TRANSFERRING SOLUTION TO AUTOCLAVES

Two-thirds of the total number of the Zircaloy-4 and Inconel specimens were precoated 3 days in 680 F degassed neutral prior to assembly.

Crevice specimens were bolted together as shown in Figure 2. A Zircaloy-4 specimen contacted Inconel on one face and a second Zircaloy-4 specimen on the other. The Inconel and Zircaloy-4 specimens were separated by a 0.004-in. Zircaloy-2 spacer inserted at one end to provide a crevice ranging from 0.004 in. to metal contact. A similar spacer separated the two Zircaloy-4 specimens and was located at the opposite end of the assembly. Inconel nuts, bolts, and support wires were used to complete the assemblies.



1X C1719

FIGURE 2. ASSEMBLED CREVICE SPECIMENS

Lighter specimen is Inconel; the two dark ones are Zircaloy-4. Note edge of Zircaloy-2 spacers between Inconel and Zircaloy-4 at top right and between Zircaloy-4 specimens at bottom left.

Each autoclave contained two precoated assemblies, one as-pickled assembly, and reference coupons of Zircaloy-4, Zircaloy-2, and Inconel. The crevice assemblies for the 750 F neutral steam test were given an additional precoat in a 3-day exposure to 680 F water adjusted to pH 10.5 with LiOH. Autoclaves were opened after 3, 14, 28, 56, and 84 days' total exposure. Reference coupons were weighed and the external surfaces of crevice specimens were examined at these times. In addition, one precoated and one as-pickled assembly from each of the steam tests were carefully opened and examined after 28 days' exposure. These specimens were then reassembled and returned to test.

Specimen Evaluation

All specimens were weighed and examined visually at low-power magnification after the corrosion tests were completed. Selected specimens also were examined metallographically and were analyzed for hydrogen. X-ray diffraction patterns were obtained of the oxide film at selected areas on several specimens.

Inconel specimens were cathodically descaled at 20 amp per dm^2 in 5 w/o sulfuric acid containing 0.5 g per liter of quinoline ethiodide inhibitor at 150 to 170 F. Specimens were dipped in 1:1 nitric acid-water after descaling to remove the lead deposited as the result of using lead anodes. Blank corrections were nil and no difficulty was experienced in descaling the Inconel.

Results

Halide Corrosion

Water Chemistry. Halide concentration and solution pH at the start and finish of each exposure period are presented in Table 2. The pH in the ammonia-treated solutions remained unchanged being above pH 10 in almost all conditions. Occasionally the pH in LiOH-treated solutions dropped to neutral during an exposure period. This effect could not be correlated with the exposure conditions and thus could not be anticipated.

Halide concentrations changed very little except in cases of autoclave leaks, excessive corrosion of the Zircaloy-4, or unexpected removal of the halide by the crud. The latter two occurred with the fluoride solutions and will be described more fully in the next section.

Corrosion Behavior. All specimens except those exposed to the 0.01 M fluoride solutions exhibited shiny black tarnish films and weight gains of less than 27 mg per dm^2 after 56 days' exposure. (Fe_3O_4 was wiped from the specimens in the crud tests.) These results compare favorably with the reported value of 26 mg per dm^2 for Zircaloy-2 after 56 days in 680 F neutral water.$^{(1)}$

Weight gains after 56 days are summarized in Table 3. In general, the as-pickled specimens had slightly higher weight gains than the precoated ones. The presence of crud in the solution and deposits on the specimens had no apparent effect on the weight gains of the precoated specimens.

Constants for the corrosion rate curves of Zircaloy-4 in these media as obtained from a log-log plot of weight gain versus time are given in Table 4. The constants compare favorably with those reported for Zircaloy-2 exposed to neutral water at 680 F.$^{(1)}$

The amount of Fe_3O_4 which deposited on specimens in crudded autoclaves varied from one test condition to another, but did not vary much within a test. As seen from Table 5, chloride solutions had the least deposition (<2 mg per dm^2) while iodide solutions had the most (up to 465 mg per dm^2). Photographs of specimens showing the extremes in crud deposition are presented in Figure 3.

The Zircaloy-4 was severely attacked in the noncrudded fluoride solutions. Photographs of the specimens are shown in Figure 4. After 3 days' exposure to LiF the precoated specimens exhibited random pitting with depths of up to 10 mils and weight

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(1) References are at end of report.

TABLE 2. WATER CHEMISTRY FOR STUDIES CONDUCTED IN AUTOCLAVES AT 680 F

Exposure Condition	0 to 3 Days				3 to 14 Days				14 to 28 Days				28 to 56 Days			
	pH		Molarity		pH		Molarity		pH		Molarity		pH		Molarity	
	Start	Finish	Start	Finish	Start	Finish	Start	Finish	Start	Finish	Start	Finish	Start	Finish	Start	Finish
LiOH																
No crud	10.5	9.5	--	--	10.5	6.7	--	--	10.8	9.7	--	--	10.8	9.5	--	--
Crud	--	--	--	--	10.5	11.3	--	--	10.8	9.5	--	--	10.8	7.0	--	--
LiF																
No crud	10.6	10.1	0.0095	0.0090	Excessive corrosion, test stopped				--	--	--	--	--	--	--	--
No crud(a)	10.8	11.4(b)	0.0010	0.0018(b)	10.8	10.8	0.0010	0.0010	10.9	11.2	0.0010	0.0010	10.6	11.2	0.0010	0.0010
Crud	--	--	--	--	10.6	6.3	0.0095	0.0008	(c)	(c)	(c)	(c)	--	--	--	--
LiCl																
No crud	10.5	9.3	0.0100	0.0094	10.7	9.9	0.0100	0.0099	10.9	10.4	0.0100	0.0097	10.8	10.4	0.0100	0.0091
Crud	--	--	--	--	10.5	6.2	0.0100	0.0088	10.9	11.4(b)	0.0100	0.0230(b)	10.8	9.6	0.0100	0.0099
LiI																
No crud	10.4	6.7	0.0110	0.0112	10.5	9.6	0.0110	0.0110	10.8	9.4	0.0110	0.0110	10.8	7.3	0.0110	0.0630(d)
Crud	--	--	--	--	10.4	11.1(b)	0.0110	0.0200(b)	10.8	6.8	0.0110	0.0107	10.8	6.4	0.0110	0.0103
NH_4OH																
No crud	10.5	10.5	--	--	10.6	10.1	--	--	10.7	10.0	--	--	10.6	10.5	--	--
Crud	--	--	--	--	10.6	10.5	--	--	10.6	10.1	--	--	10.6	10.9	--	--
NH_4F																
No crud	10.5	10.5	0.0095	0.0068	Excessive corrosion, test stopped				--	--	--	--	--	--	--	--
No crud(a)	10.6	10.4	0.0001	0.0001	10.6	10.3	0.0001	0.0001	10.6	9.3	0.0001	0.00013	10.6	9.5	0.0001	0.00013
Crud	--	--	--	--	10.5	10.2	0.0095	0.0010	(c)	(c)	(c)	(c)	--	--	--	--
NH_4Cl																
No crud	10.5	10.4	0.0099	0.0096	10.5	10.5	0.0099	0.0099	10.6	10.1	0.0099	0.0098	10.6	10.6	0.0099	0.0101
Crud	--	--	--	--	10.5	10.6	0.0099	0.0098	10.6	10.2	0.0099	0.0095	10.6	6.4	0.0099	0.0086
NH_4I																
No crud	10.5	9.7	0.0110	0.0112	10.5	10.3	0.0110	0.0113	10.6	10.1	0.0110	0.0110	10.6	10.3	0.0110	0.0109
Crud	--	--	--	--	10.5	10.2	0.0110	0.0102	10.6	10.5	0.0110	0.0108	10.6	10.3	0.0110	0.0111

(a) Tests were conducted in 0.001 M LiF and 0.0001 M NH_4F to determine whether these solutions were corrosive in the absence of crud.

(b) Slow leak in autoclaves.

(c) Crud (Fe_3O_4) concentration reduced from 100 g per liter to 1 g per liter and specimens were exposed an additional 7 days. Specimens corroded excessively and were then removed from test.

(d) Autoclave leaked during final hour of exposure.

TABLE 3. WEIGHT-GAIN DATA FOR ZIRCALOY-4 EXPOSED 56 DAYS TO 680 F pH 10.5 HALIDE SOLUTIONS [(a)]

Exposure Condition	Weight Gain, mg per dm^2[(b)]		
	No Crud		With Crud
	Bare[(c)]	Precoated[(d)]	Precoated[(d)]
LiOH	22	20	19
0.01 M LiCl	25	17	17
0.01 M LiI	26	16	19
0.001 M LiF	27	24	--
NH_4OH	18	16	17
0.01 M NH_4Cl	22	17	20
0.01 M NH_4I	23	19	15
0.0001 M NH_4F	33	25	--

(a) Reported(1) weight gain for Zircaloy-2 exposed 56 days to neutral 680 F water is 26 mg per dm^2.

(b) Weight gains obtained after wiping with a soft cloth.

(c) One specimen.

(d) Average of three specimens.

TABLE 4. CORROSION RATE CONSTANTS FOR ZIRCALOY SPECIMENS EXPOSED 56 DAYS TO 680 F pH 10.5 HALIDE SOLUTIONS

Exposure Condition	Rate Constants[(a)]			
	As-Pickled Specimens		Precoated Specimens	
	k	n	k	n
		Zircaloy-4		
LiOH	6.6	0.29	4.6	0.38
0.001 M LiF	12.5	0.20	9.1	0.24
0.01 M LiCl	7.7	0.31	5.0	0.32
0.01 M LiI	10.0	0.27	4.0	0.48
NH_4OH	5.2	0.36	4.8	0.34
0.0001 M NH_4F	6.6	0.38	6.4	0.33
0.01 M NH_4Cl	7.4	0.27	4.8	0.31
0.01 M NH_4I	8.8	0.27	4.6	0.38
		Zircaloy-2		
LiOH	7.2	0.30	--	--
NH_4OH	6.2	0.38	--	--
Neutral Water[(b)]	5.9	0.33	--	--

(a) From the empirical equation

$$w = kt^n,$$

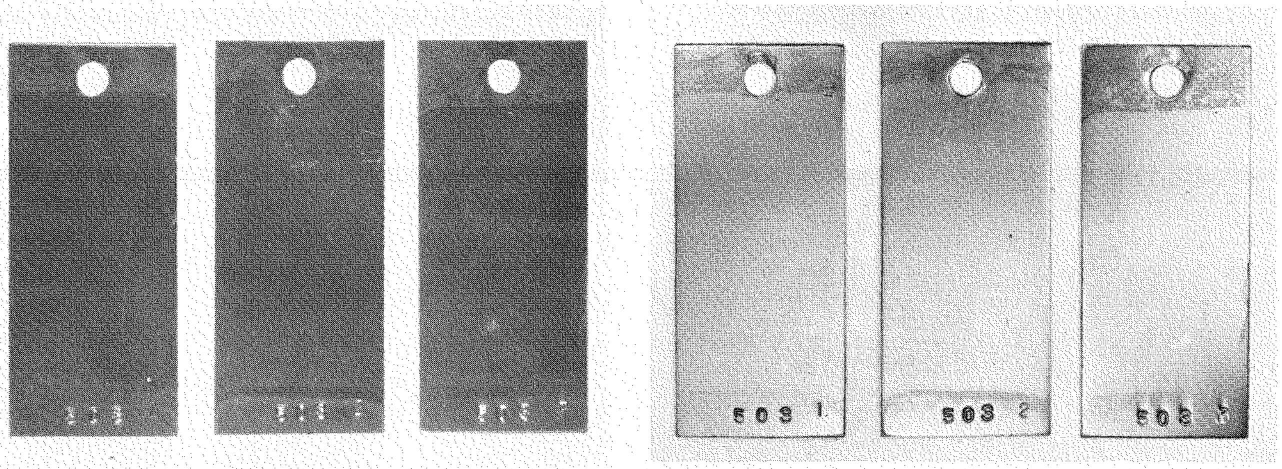
where w = total weight gain, mg per dm^2
t = time, days
k and n = constants.

(b) From Reference (1).

TABLE 5. Fe_3O_4 (CRUD) DEPOSITED ON ZIRCALOY SPECIMENS EXPOSED 56 DAYS TO 680 F pH 10.5 HALIDE SOLUTIONS

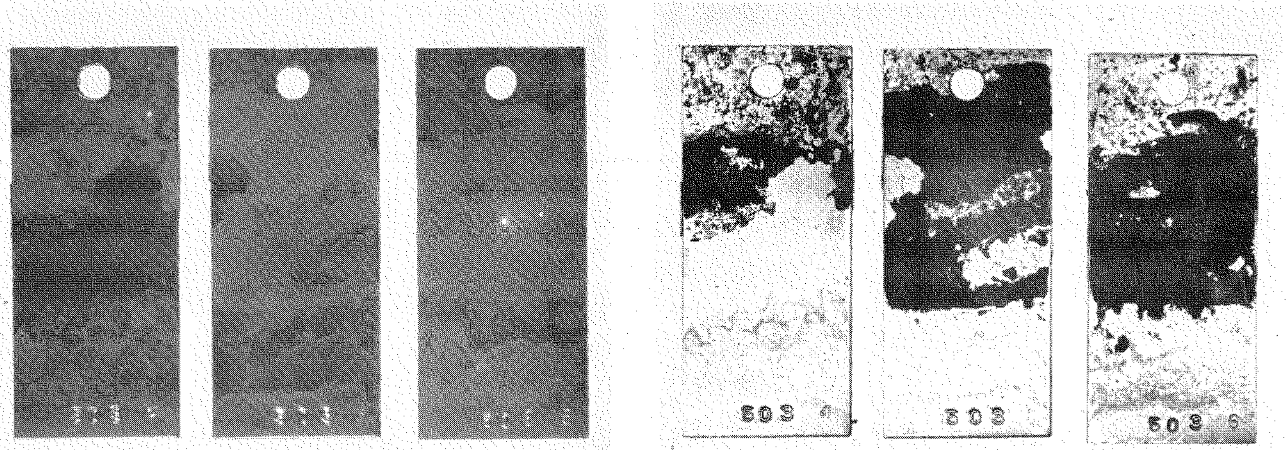
Exposure Condition	Weight[(a)], mg per dm^2
LiOH	111
	117
	148
NH_4OH	40
	41
	57
0.01 M LiCl	2
	1
	2
0.01 M LiI	114
	165
	170
0.01 M NH_4Cl	1
	1
	1
0.01 M NH_4I	465
	376
	336

(a) Each figure is for one specimen.



1X Oblique Lighting C1660 1X Vertical Lighting C1661

a. Exposed to 0.01 M NH_4Cl

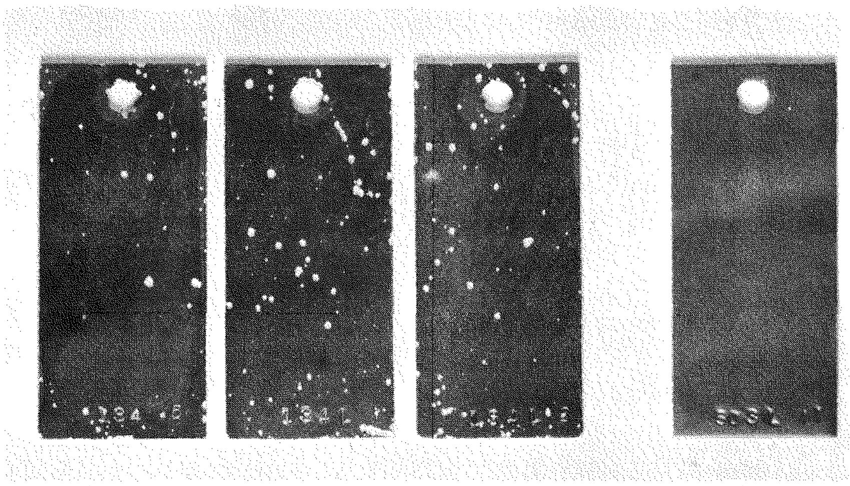


1X Oblique Lighting C1662 1X Vertical Lighting C1663

b. Exposed to 0.01 M NH_4I

FIGURE 3. PHOTOGRAPHS DEPICTING EXTREMES IN AMOUNT OF CRUD DEPOSITED ON ZIRCALOY-4 EXPOSED 56 DAYS TO 680 F HALIDE SOLUTIONS

Gray areas under oblique lighting are crud and correspond to the black areas in the photograph of the same specimens under vertical lighting.



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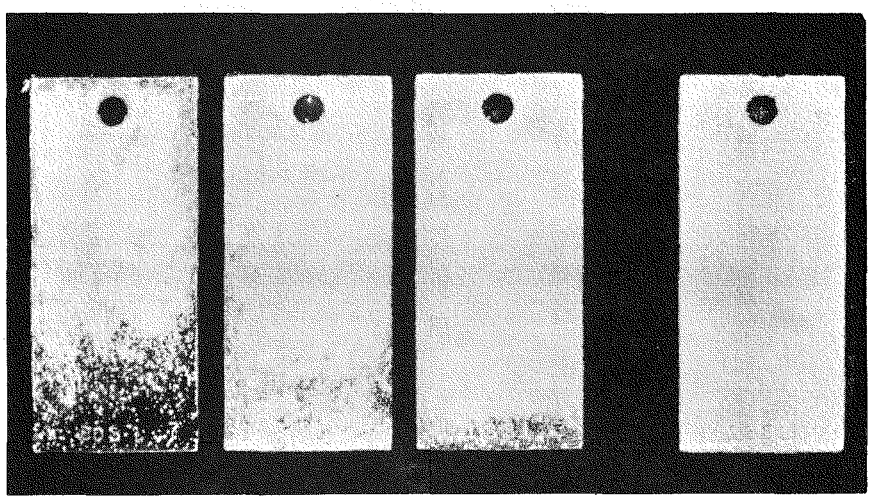
a. Exposed to 0.01 M LiF

Precoated specimens at
left, as-pickled specimen
at right.



1X C1569

b. Exposed to 0.01 M NH_4F

Precoated specimens at
left, as-pickled specimen
at right.

FIGURE 4. APPEARANCE OF ZIRCALOY-4 SPECIMENS AFTER 3 DAYS' EXPOSURE TO 680 F pH 10.5 FLUORIDE SOLUTIONS

White spots on precoated specimens in LiF are pits.

losses ranging from 64 to 154 mg per dm^2. A cross section through one of the pits is shown in Figure 5. The as-pickled specimen had an adherent tan film and a weight gain of 364 mg per dm^2. In NH_4F the precoated specimens were covered with heavy loosely adherent oxide over most of their surface while the as-pickled specimen was completely covered with white oxide. Weight losses for the precoated specimens ranged from 440 to 2450 mg per dm^2, while the loss for the as-pickled specimen was 5810 mg per dm^2.

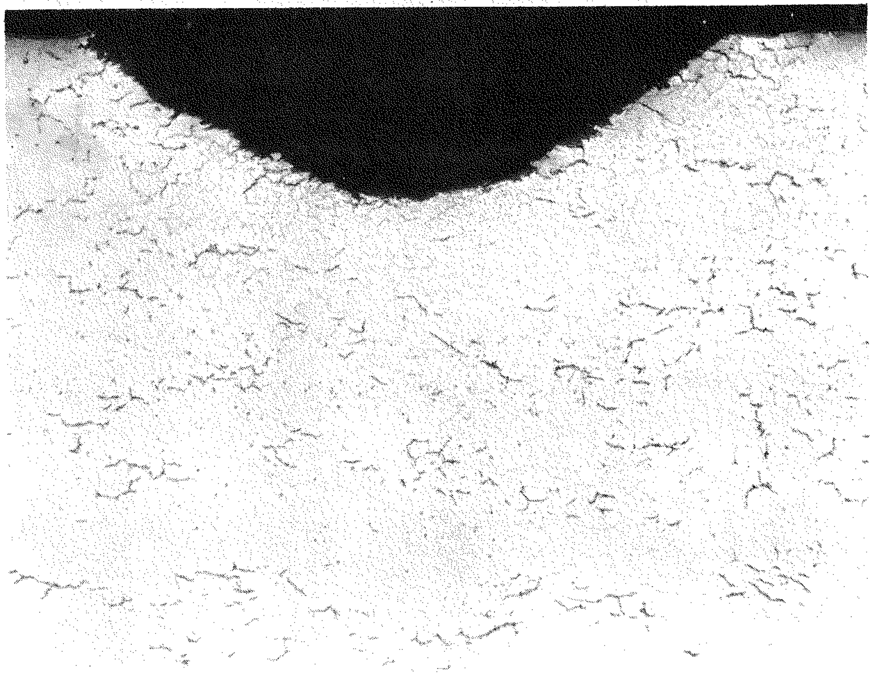


FIGURE 5. CROSS SECTION THROUGH A TYPICAL PIT IN PRECOATED ZIRCALOY-4 SPECIMEN EXPOSED 3 DAYS TO 680 F pH 10.5 0.1 M LiF

Specimen 134L-1 from Figure 4 is shown here. Note the absence of hydride buildup at the bottom of the pit. Etchant was lactic-nitric-hydrofluoric acids.

Chemical analysis of the white oxide formed on Zircaloy-4 in NH_4F revealed 0.7 and 0.4 w/o fluoride on the as-pickled and precoated specimens, respectively. This could account for the fluoride depletion in this test (see Table 2).

The Zircaloy-4 exposed to crudded fluoride had a shiny black film and showed no evidence of unusual attack after 14 days' exposure. However, the fluoride concentration dropped to 0.001 M (from 0.01 M, see Table 2). Extraction analysis revealed fluoride contents of 1.8 mg per g and 0.25 mg per g in the crud from the LiF and NH_4F tests, respectively. The former is sufficiently large to account for the 0.009 mole LiF missing from solution.

The above Zircaloy-4 specimens were then exposed to 0.01 M fluoride with the crud content reduced to 1 g per liter (from 100 g per liter). After 7 days' exposure they showed the same type of attack as those exposed to crud-free solutions. The appearance of the specimens is shown in Figure 6. Note the similarity to the photographs in Figure 4.

Tests were conducted in 0.001 M LiF and 0.0001 M NH_4F to determine whether these solutions were corrosive in the absence of crud. Specimens maintained a shiny black tarnish film and had weight gains of less than 33 mg per dm^2. Data for these specimens are included in Tables 2, 3, and 4.

Hydrogen Pickup. Representative samples in each test condition were analyzed for hydrogen after corrosion. On the assumption that the hydrogen content of an as-machined specimen was representative of that present before corrosion, hydrogen pickups were determined and related to the quantity of hydrogen produced by the corrosion reaction. These results are presented in Table 6. In general, the hydrogen absorbed by the pickled specimens was greater, in amount and per cent of that theoretically available, than that absorbed by the precoated specimens.

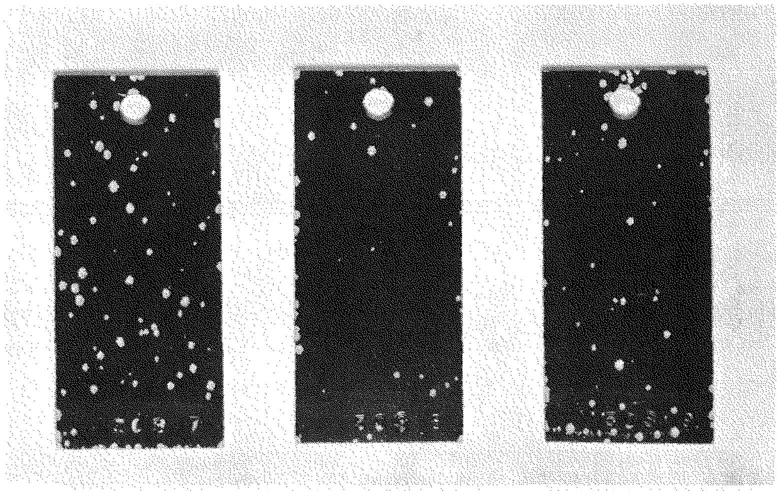
The specimens which were exposed to the 0.01 M fluorides and experienced heavy corrosion attack exhibited high hydrogen pickup. Different areas in some of the specimens varied in hydrogen content depending on whether the surface was covered with a white or dark oxide. This is evident from the data in Table 6 and the photomicrographs in Figures 7 and 8. Note the high concentration of hydride platelets in the areas beneath the white oxide. Photomicrographs of as-received Zircaloy-4 and a specimen from the chloride tests, which are also typical of those from the iodide tests, are shown in Figure 9 for comparison.

Crevice Corrosion

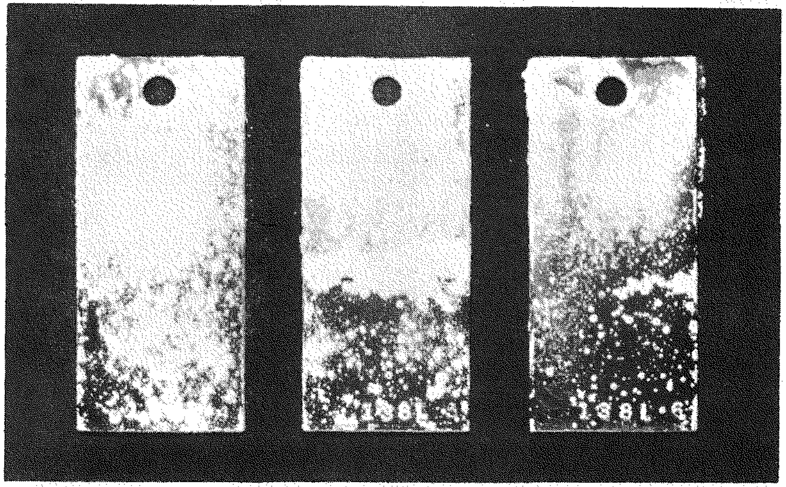
Water Chemistry. The pH was maintained in the 680 F water tests and was greater than 10 after each exposure. The pH of the steam condensate from the 750 F neutral steam test ran about 6.8 while that from the NH_4OH steam test ran 10.4 to 10.6.

Corrosion Behavior. After 84 days' exposure the external surfaces of Inconel specimens were covered with a straw-colored tarnish while those of Zircaloy-4 were shiny black at 680 F and milky at 750 F. The mating faces of Inconel had areas of dark iridescent tarnish. Those surfaces of Zircaloy-4 which were in direct contact with Inconel exhibited small areas of white corrosion product. Faint brown staining was observed in the area of direct contact between Zircaloy-4 specimens. No unusual attack was observed on the Zircaloy-4 at the Zircaloy-2 spacers, although the latter were milky. The only accelerated corrosion noted in the crevice area was some faint white oxide on the Zircaloy-4 which was coupled to Inconel in the 750 F steam tests started with ammonia-treated water. Photographs of these specimens are shown in Figure 10 along with those of typical specimens from the 680 F tests.

X-ray diffraction patterns of the white, tan, and black oxides revealed them all to be monoclinic ZrO_2. (However, as much as 5 to 15 per cent of some other oxide would be undetected by this analysis technique.)



a. Exposed to 680 F 0.01 M LiF



b. Exposed to 680 F 0.01 M NH_4F

FIGURE 6. APPEARANCE OF ATTACK WHICH OCCURRED ON PRECOATED ZIRCALOY-4 DURING THE 7-DAY EXPOSURE WHEN THE Fe_3O_4 (CRUD) CONCENTRATION OF THE FLUORIDE SOLUTIONS WAS REDUCED FROM 100 TO 1 G PER LITER

Note the similarity to Figure 4.

TABLE 6. HYDROGEN PICKUP IN ZIRCALOY-4 SPECIMENS EXPOSED 56 DAYS TO 680 F HALIDE SOLUTIONS AT pH 10.5

			Hydrogen(b)		
				Weight Gain	
Specimen(a) Preparation	Exposure Condition	Oxygen Weight Gain(b), mg per dm^2	Total, ppm	Mg per Dm^2	Per Cent of Theoretical
Machined	None	--	22	--	--
Precoated	None	12	27	0.22	15
Pickled	LiOH, no crud	25	35	0.49	16
Precoated	LiOH, no crud	21	24	0.083	3
	LiOH, crud	19	24	0.079	3
Pickled	NH_4OH, no crud	18	32	0.35	16
Precoated	NH_4OH, no crud	15	23	0.039	2
	NH_4OH, crud	18	22	0	--
Pickled	0.01 M LiF, no crud	346(c)	513	17.8	41
Precoated	0.01 M LiF, no crud	-152(c)	95	3.04	--
	0.01 M LiF, crud	-188(d)	105	3.44	--
Pickled	0.001 M LiF, no crud	27	34	0.52	15
Precoated	0.001 M LiF, no crud	24	28	0.26	9
Pickled	0.01 M LiCl, no crud	25	31	0.35	12
Precoated	0.01 M LiCl, no crud	18	33	0.44	20
	0.01 M LiCl, crud	14	23	0.041	2
Pickled	0.01 M LiI, no crud	25	36	0.53	16
Precoated	0.01 M LiI, no crud	24	23	0.041	1
	0.01 M LiI, crud	19	27	0.20	8
Pickled	0.01 M NH_4F, no crud	-5810(c)	2410	91.7	--
Precoated	0.01 M NH_4F, no crud	-442(c)	454	17.6	--
	0.01 M NH_4F, crud(e)	-2700(d)	1300	53.0	--
	0.01 M NH_4F, crud(f)	-2700(d)	567	23.1	--
Pickled	0.0001 M NH_4F, no crud	32	44	0.98	24
Precoated	0.0001 M NH_4F, no crud	24	36	0.62	21
Pickled	0.01 M NH_4Cl, no crud	22	30	0.31	11
Precoated	0.01 M NH_4Cl, no crud	16	23	0.041	2
	0.01 M NH_4Cl, crud	22	20	0	--
Pickled	0.01 M NH_4I, no crud	23	36	0.48	17
Precoated	0.01 M NH_4I, no crud	21	32	0.43	16
	0.01 M NH_4I, crud	17	21	0	--

(a) Precoated 3 days in 680 F neutral high-purity water.

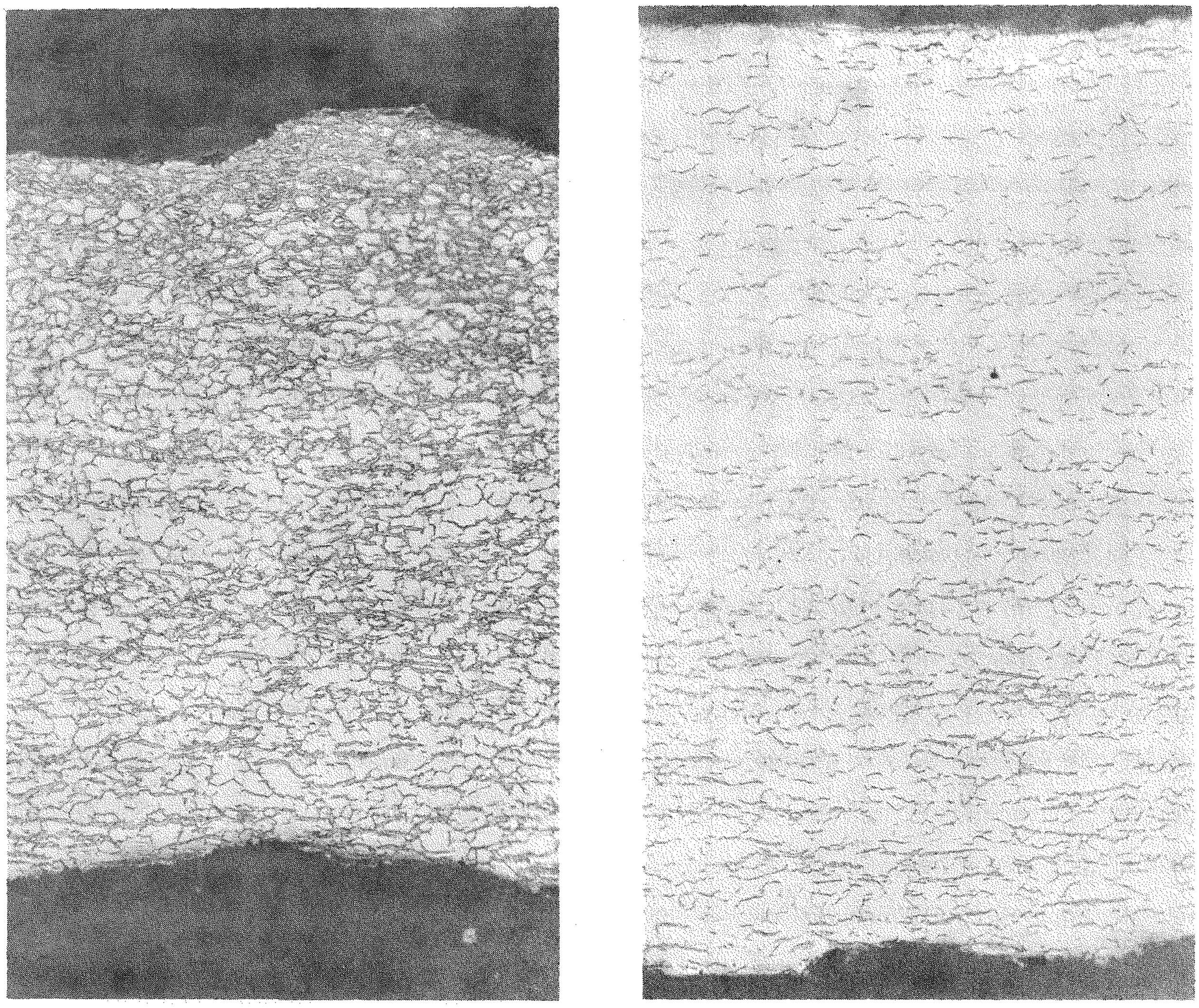
(b) Includes weight gained during precoating.

(c) Exposed 3 days only.

(d) Exposed 14 days to crud conditions, then crud level was reduced to 1 g per liter (from 100 g per liter) during additional 7-day exposure.

(e) White area from specimen 138L-6 shown at right in Figure 6b.

(f) Black area from Specimen 138L-6 shown at right in Figure 6b.

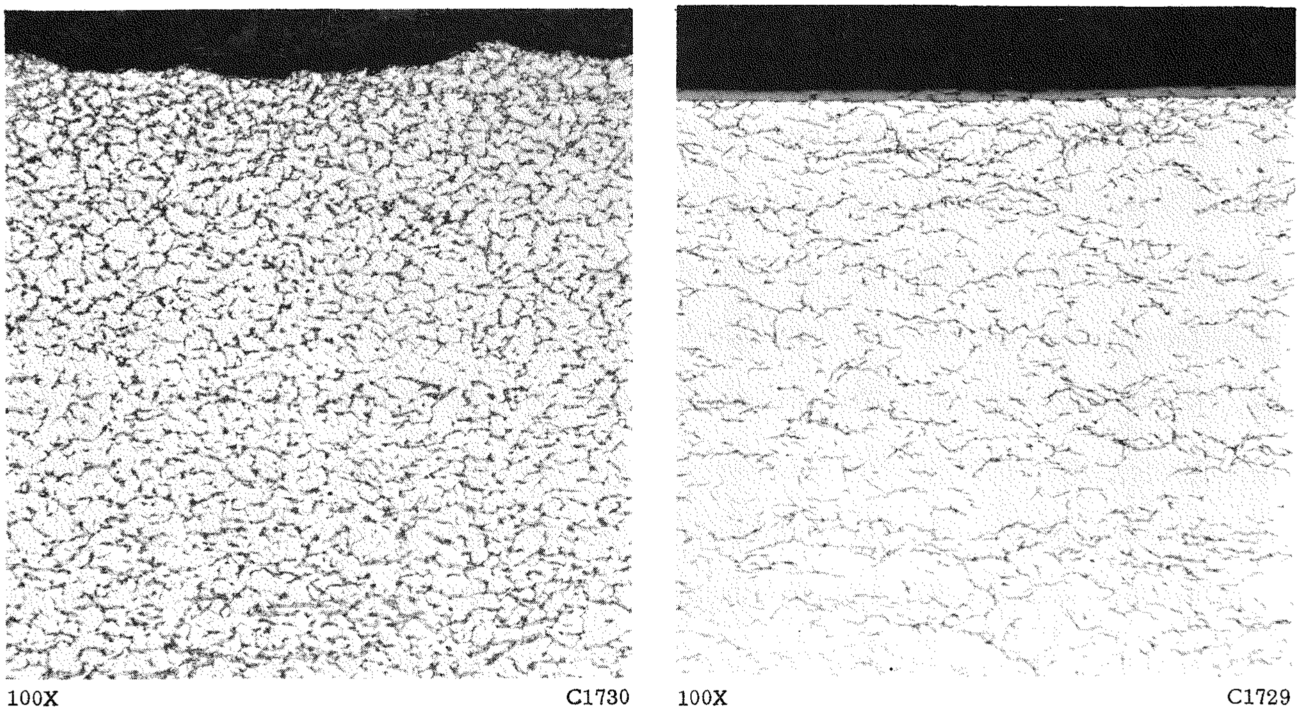


a. Beneath White Oxide (1300 PPM of Hydrogen)

b. Beneath Black Oxide (567 PPM of Hydrogen)

FIGURE 7. CROSS SECTIONS OF A ZIRCALOY-4 SPECIMEN EXPOSED TO 680 F 0.01 M NH_4F AT pH 10.5

Lower right-hand specimen from Figure 6 is shown here. Note heavier concentration of hydride platelets beneath the white oxide and areas of heavy attack. Etchant was lactic-nitric-hydrofluoric acids.

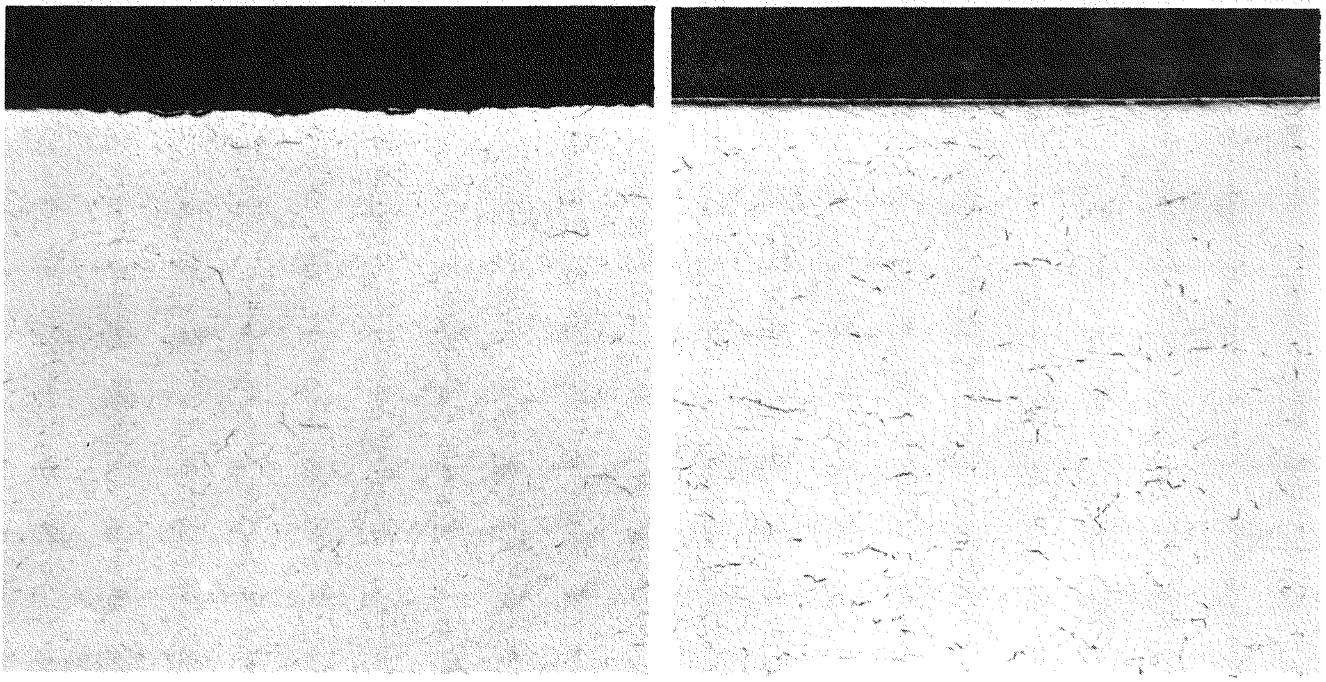


a. NH_4F (2700 PPM of Hydrogen)

b. LiF (513 PPM of Hydrogen)

FIGURE 8. CROSS SECTIONS OF PICKLED ZIRCALOY-4 EXPOSED 3 DAYS TO 680 F pH 10.5 FLUORIDE SOLUTIONS

Note heavy hydride concentration in photomicrograph at left as the result of more severe corrosion of this specimen. Etchant was lactic-nitric-hydrofluoric acids.

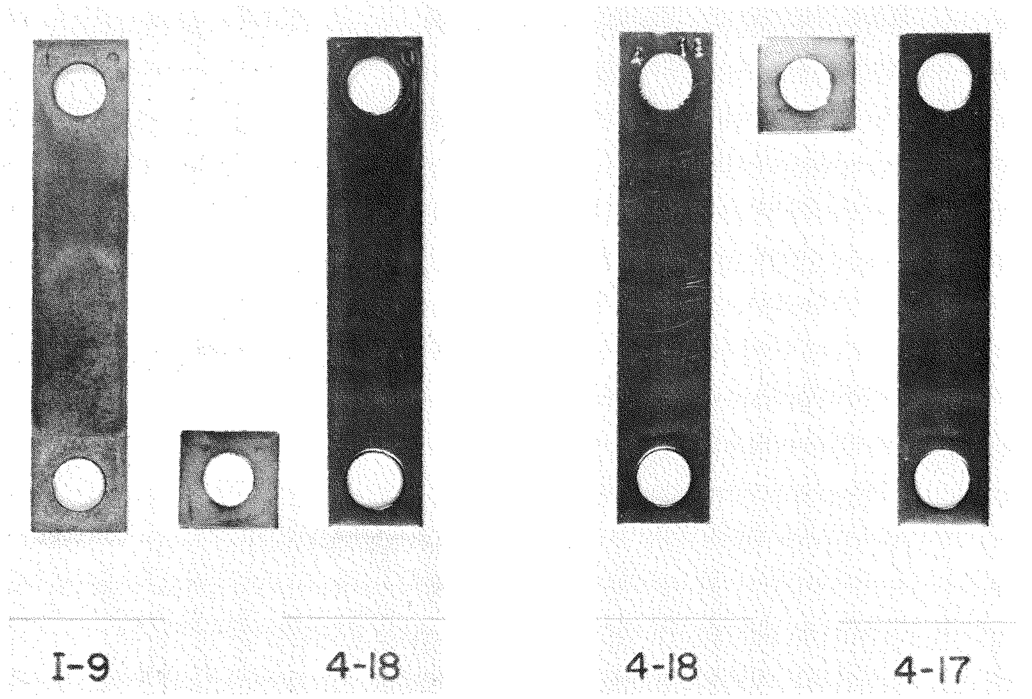


a. As Machined (22 PPM of Hydrogen)

b. Pickled Plus 56 Days' Exposure to 680 F pH 10.5 NH_4Cl (30 PPM of Hydrogen)

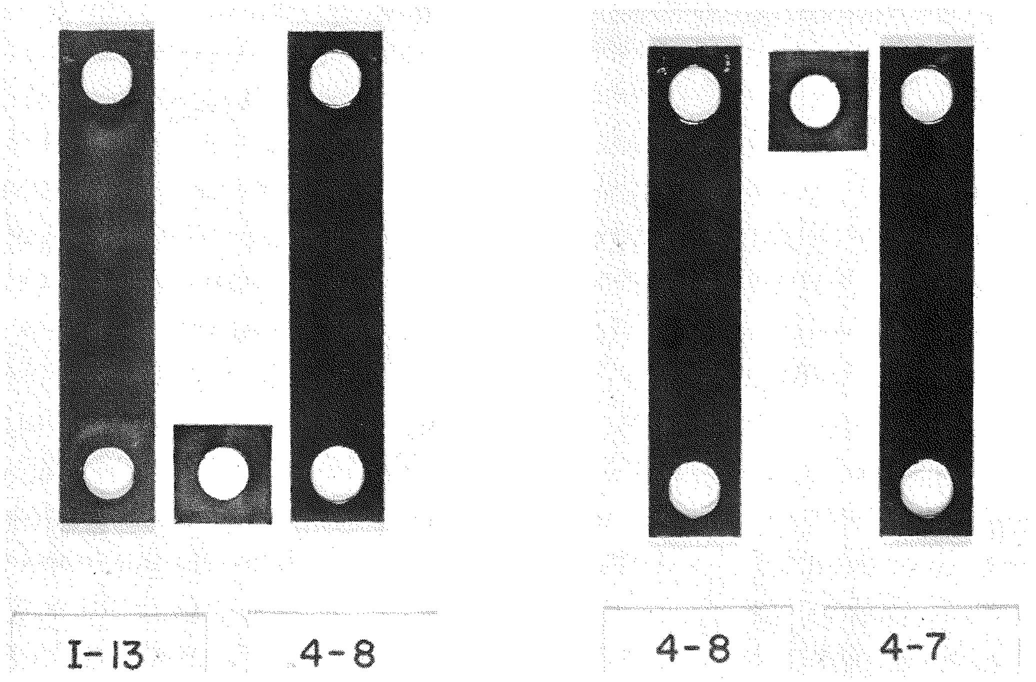
FIGURE 9. APPEARANCE OF HYDRIDE PLATELETS IN AS-MACHINED ZIRCALOY-4 SPECIMEN AND A TYPICAL SPECIMEN EXPOSED TO 680 F HALIDE SOLUTIONS

Compare with Figures 8 and 9. Etchant was lactic-nitric-hydrofluoric acids.



1X Inconel to Zircaloy-4 C1631 1X Zircaloy-4 to Zircaloy-4 C1632

a. Exposed 28 Days to 750 F Steam Produced From pH 10.5 NH_4OH



1X Inconel to Zircaloy-4 C1716 1X Zircaloy-4 to Zircaloy-4 C1717

b. Exposed 84 Days to 680 F pH 10.5 NH_4OH

FIGURE 10. APPEARANCE OF MATING FACES OF CREVICE SPECIMENS AFTER EXPOSURE TO 680 F WATER AND 750 F STEAM

Note faint white oxide on Zircaloy-2 spacers and the Zircaloy-4 which contacted Inconel.

Four oxide streaks were observed in the crevice area of one Zircaloy-4 specimen bolted to Zircaloy-4 and exposed to 680 F LiOH-treated water. Photographs of these streaks are shown in Figure 11. Close examination of the streaks indicated they were voids with a thin oxide coating on the walls of the void. A cross section through one of the voids is shown in Figure 12. The voids did not appear to be a result of corrosion but apparently were present in the original rolled sheet. This conclusion is based on the observations of the small amount of corrosion product in the voids, the small number of hydride platelets in the microstructure, the low hydrogen analysis of the specimen (see Table 8), and the low weight gain of the specimen. The latter two were 25 ppm and 23 mg per dm^2, respectively, compared with average values of 26 ppm and 22 mg per dm^2, respectively, for duplicate specimens exposed to this condition.

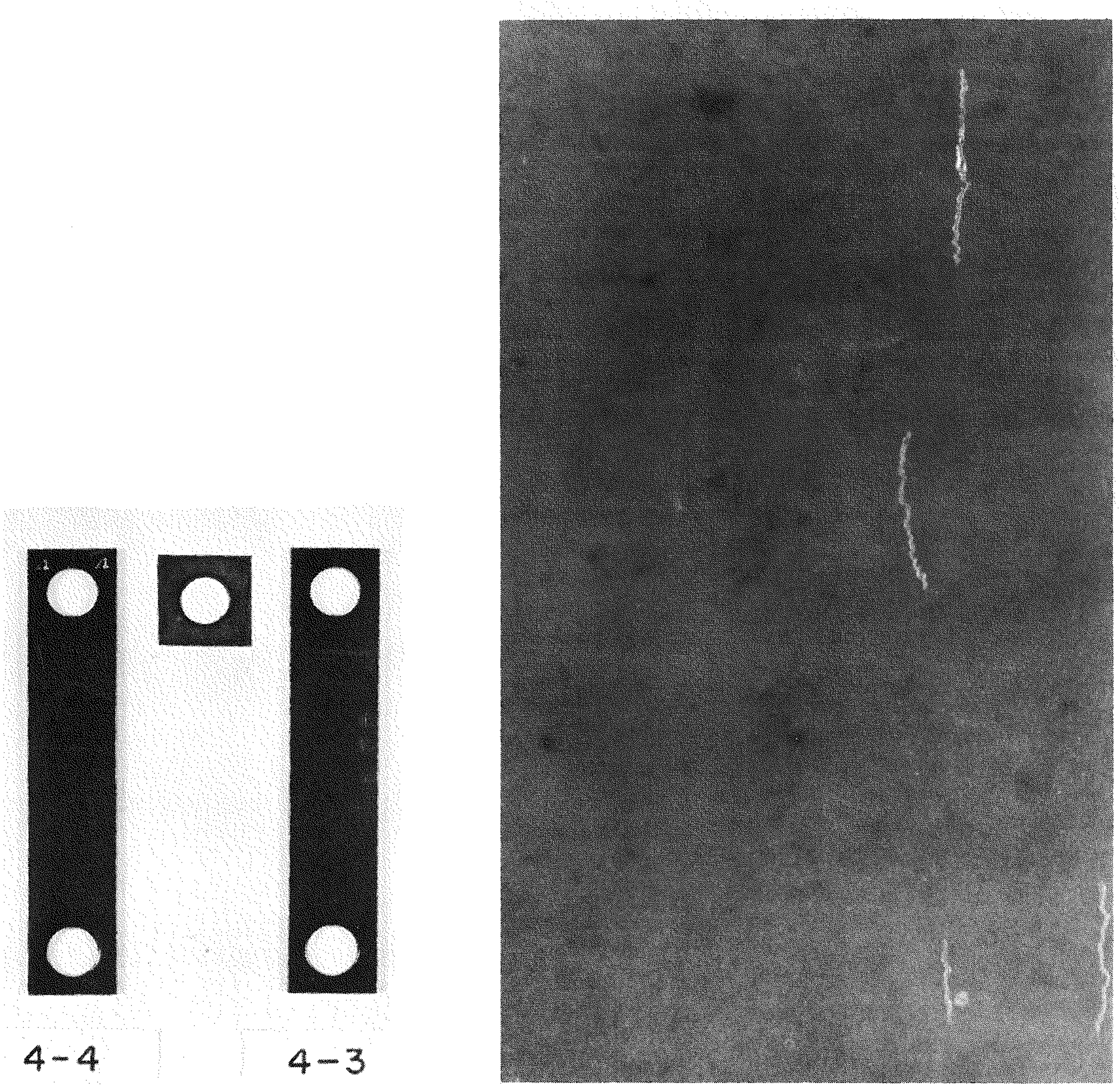
Weight changes for the crevice specimens and the reference coupons are presented in Table 7. With one or two exceptions there was good duplication among specimens in a given exposure condition. Whether crevice specimens were exposed in the as-pickled or precoated condition had little or no effect on weight gain.

TABLE 7. WEIGHT-CHANGE RESULTS FOR CREVICE SPECIMENS EXPOSED 84 DAYS TO HIGH-TEMPERATURE WATER AND STEAM

	Weight Change, mg per dm^2			
Specimen	680 F pH 10.5 LiOH	680 F pH 10.5 NH_4OH	750 F 1500-PSI Neutral Steam	750 F 1500-PSI NH_3 Steam
Zircaloy-4 crevice(a)	22	25	52	47
Zircaloy-4 reference(b, c)	16	7	34	34
Zircaloy-2 reference(b)	28	32	54	49
Inconel crevice(d)	-12	-11	-11	-9
Inconel reference(b)	-18	-27	-32	-27

(a) Average of six specimens.
(b) One specimen.
(c) Weight changes were erratic.
(d) Average of three specimens.

Although the Zircaloy-4 specimens in the 750 F steam tests were milky after 84 days' exposure, their weight gains of about 50 mg per dm^2 were considerably lower than the reported value of 96 mg per dm^2 for Zircaloy-2 exposed to neutral steam(1). The low weight gains may have been related to the "memory effect" which has been observed for Zircaloy-2 when transferred from one test temperature to another(2). (The specimens in the steam tests were first exposed to 680 F water.) The Zircaloy-2 and Zircaloy-4 reference coupons also exhibited low weight gains. Those of the latter were somewhat erratic, possibly because of the small specimen size.



1X C1724
a. Components After Exposure

15X C1725
b. Enlarged Area of Specimen 4-3

FIGURE 11. APPEARANCE OF VOIDS ON MATING FACE OF ONE ZIRCALOY-4 CREVICE SPECIMEN EXPOSED 84 DAYS TO 680 F WATER ADJUSTED TO pH 10.5 WITH LiOH

The voids are located at the right edge and near the middle of Specimen 4-3 in the photograph at left.

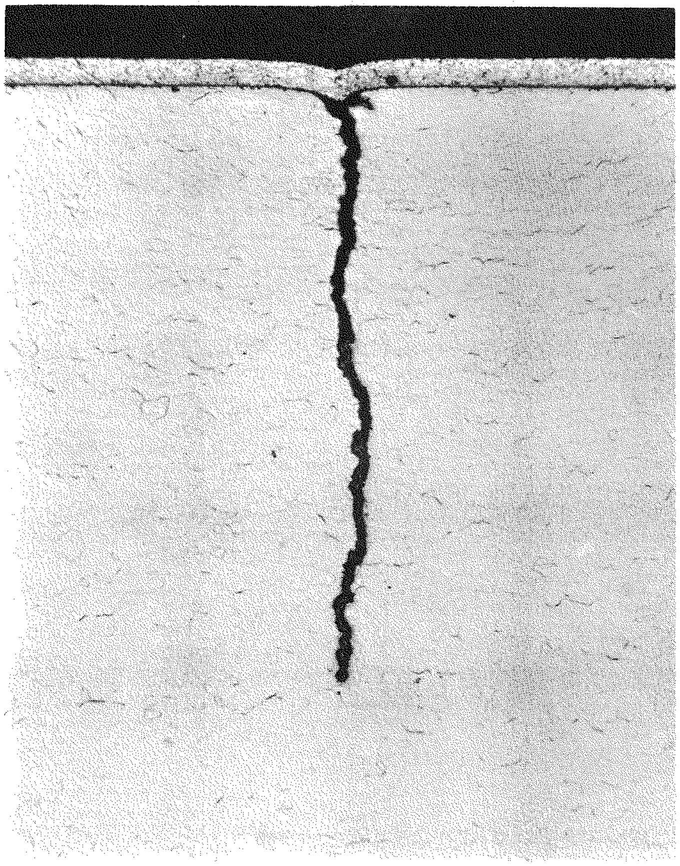

100X C1726

FIGURE 12. CROSS SECTION THROUGH THE TOP VOID IN THE ZIRCALOY-4 SPECIMEN SHOWN IN FIGURE 11

This specimen analyzed 25 ppm of hydrogen. The layer on the surface is backing foil used to prevent edge rounding. Note the absence of heavy oxide buildup in the void and the small number of hydride platelets in the structure. Etchant was lactic-nitric-hydrofluoric acids.

Descaled weight changes for the Inconel crevice specimens ran about 10 mg per dm^2 for all test conditions after the 84 days' exposure. Descaled weights of the reference coupons were 2 to 3 times as high. However, the latter specimens exhibited some intergranular attack and grain removal from the pickling solution. Additional grains may have been removed as the result of corrosion and the blasting action of hydrogen during descaling. The reference coupons were only about one-half as thick as the crevice coupons. If they had been reduced by hot working they may have been in a heat-treated condition which could make them more susceptible to attack by the pickling solution. Examination of the microstructures failed to reveal any significant differences in the type and amount of grain-boundary precipitate in the two types of specimens.

Hydrogen Pickup. Hydrogen pickup for Zircaloy-4 specimens from the four exposure conditions is summarized in Table 8. In 680 F water the hydrogen pickup was low and represented only 6 to 10 per cent of that theoretically available from the corrosion reaction. Hydrogen absorption in 750 F steam also was low with theoretical percentages ranging from 9 to 20 per cent.

Selected specimens were mounted and examined in cross section along their entire length. Hydride platelets were distributed uniformly throughout the microstructure and had the appearance of the photomicrograph on the right in Figure 9. No unusual attack or hydride concentration was observed in the vicinity of the oxide spots near the end of the Zircaloy-4 specimens which contacted Inconel.

DISCUSSION

Halide Corrosion

The results of the study have shown that the corrosion behavior of Zircaloy-4 in high-temperature water is not affected by up to 0.01 M chloride or iodide contamination in the water. The presence of a synthetic crud deposit apparently has little or no effect on corrosion behavior in these solutions.

Hydrogen pickup by the Zircaloy-4 was low in the chloride and iodide solutions, although precoated specimens appeared to absorb a lower percentage of the theoretically available hydrogen than did the as-pickled specimens. The reason for the low pickup in precoated specimens is not clear. It has been shown that the oxide coating which is formed on Zircaloy-4 in neutral high-purity 680 F water (the precoating condition) results in absorption of 15 to 20 per cent of the theoretical hydrogen(3). Thus, the retarding effect cannot be attributed to the oxide barrier alone. On the other hand, the nature of the solution cannot, by itself, be responsible for the low hydrogen pickup, because the as-pickled specimens absorbed 15 to 20 per cent of the theoretical hydrogen. If it is a solution effect, it probably is related to high pH rather than halide content, because hydrogen pickup behavior was similar in halide and halide-free solutions, and the common factor in both solutions was high pH. Thus, it would appear from these limited results that the oxide film formed on Zircaloy-4 during precoating in neutral 680 F high-purity water was a barrier to hydrogen absorption during subsequent exposure to high pH 680 F water.

TABLE 8. HYDROGEN PICKUP IN ZIRCALOY-4 CREVICE SPECIMENS EXPOSED 84 DAYS TO HIGH-TEMPERATURE WATER AND STEAM

Specimen Preparation	Exposure Condition	Oxygen Weight Gain(a), mg per dm^2	Hydrogen(a) Total, ppm	Hydrogen(a) Weight Gain Mg per Dm^2	Hydrogen(a) Weight Gain Per Cent of Theoretical
Machined	None	--	22	--	--
Pickled	680 F LiOH pH 10.5 water	30	28	0.34	9
Precoated(b)	Ditto	21	26	0.23	9
Precoated(b, c)	Ditto	23	25	0.16	6
Pickled	680 F NH_4OH pH 10.5 water	22	27	0.28	10
Precoated(b)	Ditto	19	26	0.23	9
Pickled	750 F steam from NH_4OH pH 10.5 water	43	37	0.84	16
	Ditto	40	39	0.91	18
Precoated(b)	Ditto	48	32	0.57	10
Precoated(d)	750 F steam from neutral water	49	44	1.22	20
	Ditto	51	37	0.84	13
Precoated(e)	Ditto	53	34	0.66	10

(a) Includes weight gained during precoating.
(b) Precoated 3 days in 680 F neutral water.
(c) Specimen with voids.
(d) Precoated 3 days in 680 F LiOH pH 10.5.
(e) Precoated 3 days in 680 F neutral water plus 3 days in 680 F LiOH pH 10.5.

Severe attack of Zircaloy-4 by 680 F lithium and ammonium fluoride solutions appears to occur at concentrations above 0.001 M. Severe attack did not occur in 0.001 M LiF or 0.0001 M NH_4F crud-free solution. (Higher than normal weight gains occurred in the 0.0001 M NH_4F which suggests that these specimens would reach transition in corrosion rate sooner than those in the other conditions.) No unusual attack was noted in the crudded solutions which originally were 0.01 M but had dropped to 0.001 M at the end of the test. In the latter, the low concentration of fluoride rather than the deposited crud appeared to be responsible for the low rate of attack, because subsequent exposure of the crud-covered specimens to almost crud-free 0.01 M fluoride resulted in severe attack.

The pitting attack on the precoated Zircaloy-4 specimens exposed to 0.01 M LiF suggests there were voids, cracks or some other imperfection in the oxide film which allowed the aggressive electrolyte to contact the metal substrate. The pitting could have been accelerated by galvanic corrosion with the oxide film being a large cathode and the exposed metal in the voids being small anodes. An analogous situation is found in the pitting of steel at breaks in the mill scale on its surface.

Attack on precoated specimens in 0.01 NH_4F was more general although some pitting did occur and metal wastage in some areas was as deep as the pitting observed in LiF (see Figures 5 and 7). The more aggressive nature of the NH_4F might be related to the lower pH (nearer neutral) of the ammoniated solution at the corrosion temperature. It has been shown with solution of about pH 9 at room temperature that NH_4OH has a lower pH at 570 F than does LiOH(4).

The mechanism by which the fluoride was removed from solution and became associated with the crud (Fe_3O_4) is not known. It was not possible to identify the nature of the fluoride in the crud because of the extremely low fluoride-to-crud ratio. However, it would appear to be related to adsorption (physical or chemisorption) of the fluoride on the crud. This is based on the observation that fluoride depletion occurred with 100 g per liter crud but not with 1 g per liter. This represents a difference of 100 to 1 in surface area available for adsorption on the crud. On the other hand, 1 g per liter crud would more than provide an excess of iron ions if an insoluble iron fluoride or iron fluoride complex were to be formed under these conditions. In any event, the phenomenon appears to occur only at elevated temperatures because room-temperature experiments conducted at varying crud levels failed to result in fluoride depletion in the solutions.

Crevice Corrosion

From the results of this program crevice-corrosion of Zircaloy-4 in high-temperature water and steam apparently is not a serious problem at crevices greater than about 0.001 in. Some areas of white or tan oxide were observed in the zones of metal-to-metal contact. The oxide was notably heavier where Zircaloy-4 contacted Inconel than where Zircaloy-4 contacted itself, but in no case was localized penetration of the metal observed. Weight gains and hydrogen absorption were comparable with those of noncrevice specimens.

The reason for the corrosion at the Inconel-to-Zircaloy-4 contact is a matter of conjecture. Changes in solution concentration in the crevice can be ruled out because of the lack of attack in the crevices of Zircaloy-4 to Zircaloy-4. Galvanic corrosion is a possibility although previous work at Battelle with Zircaloy-2 revealed no unusual corrosion between Inconel and Zircaloy-2 bolt couples in 550 F ammonia-treated water(5).

Another possibility is fluoride contamination from the pickled surface of the Inconel. It was shown that some incipient grain-boundary attack occurred during the pickling of the Inconel in $HF-HNO_3$ in preparing the corrosion specimens. Nickel fluoride, one of the possible products of the pickling, is only slightly soluble in cold water and may not have been completely removed from the slightly etched grain boundaries. This fluoride in close proximity to the Zircaloy-4 in the crevice assemblies could cause some attack of the Zircaloy-4. This explanation could also account for the faint white oxide observed over the entire crevice area of the as-pickled Zircaloy-4 coupled to as-pickled Inconel in the one steam test. Failure to detect fluoride by X-ray diffraction of the corrosion products in these localized areas does not rule out this possibility, since this means of identification will usually not detect less than 5 per cent of a constituent.

In practice, the fluoride contamination possibility could be avoided by using some means of preparing the Inconel surface with other than the $HF-HNO_3$ pickle, or finding suitable rinsing procedures if the pickle is used.

CONCLUSIONS

The following conclusions can be made based on the methods employed and the results obtained from this study.

(1) The corrosion resistance of Zircaloy-4 in 680 F pH 10.5 water is unaffected by chloride or iodide contaminations of 0.01 M concentration and deposits of Fe_3O_4 on the Zircaloy-4 surface do not accelerate corrosion in these halide solutions.

(2) Zircaloy-4 begins to exhibit accelerated attack as the fluoride concentration is increased from 0.001 to 0.01 M in 680 F pH 10.5 water.

(3) Surface deposits of Fe_3O_4 do not appear to increase or retard corrosion on Zircaloy-4 in 680 F 0.01 M fluoride solutions, although large quantities of Fe_3O_4 remove fluoride from solution and thereby decrease corrosion attack.

(4) Crevice corrosion of Zircaloy-4 does not appear to be a serious problem in 680 F water or 750 F steam.

ACKNOWLEDGMENT

This work was conducted under Reference No. 804R for Knolls Atomic Power Laboratory operated for the Atomic Energy Commission by the General Electric Company. Liaison was maintained with Messrs. R. J. Enrico and W. K. Anderson of that laboratory, whose assistance and suggestions have been greatly appreciated.

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