EXTERNAL TRANSMITTAL
AUTHORIZEDOAK RIDGE NATIONAL LABORATORY
Operated by
UNION CARBIDE NUCLEAR COMPANY
Division of Union Carbide Corporation Post Office Box X
Oak Ridge, Tennessee

MASTER

ORNL
CENTRAL FILES NUMBER

58-10-95

DATE: October 31, 1958

SUBJECT: Quarterly Report of the Solution Materials Section for the Period
Ending October 31, 1958

TO: E. G. Bohlmann

FROM: J. C. Griess, H. C. Savage, R. S. Greeley, J. L. English, S. E. Bolt,
D. N. Hess, P. D. Neumann, E. S. Snavely, W. C. Ulrich, and N. E. Wisdom

COPY NO. 170

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report.

The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

DISCLAIMER

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

DISCLAIMER

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

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares; handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

Reports previously issued in this series are as follows:

ORNL CF 56-1-167	Period Ending January 31, 1956
ORNL CF 56-4-138	Period Ending April 30, 1956
ORNL CF 56-7-52	Period Ending July 31, 1956
ORNL CF 56-10-13	Period Ending October 31, 1956
ORNL CF 57-1-144	Period Ending January 31, 1957
ORNL CF 57-4-55	Period Ending April 30, 1957
ORNL CF 57-7-121	Period Ending July 31, 1957
ORNL CF 57-10-80	Period Ending October 31, 1957
ORNL CF 58-1-72	Period Ending January 31, 1958
ORNL CF 58-4-131	Period Ending April 30, 1958
ORNL CF 58-7-132	Period Ending July 31, 1958

CONTENTS

	<u>Page No.</u>
I. SUMMARY	5
II. INTRODUCTION	7
III. 100A LOOP PROGRAM	8
A. Second-Phase Behavior of Dilute Uranyl Sulfate Solutions	8
B. Stability of Dilute Uranyl Sulfate Solutions Containing Alkali or Alkaline-Earth Sulfates	14
C. Stress-Corrosion Cracking Tests in Water at 200°C with Phosphate and Fluoride	16
D. Effect of Cold Work and Heat Treatment on Corrosion of Type 347 Stainless Steel	21
E. Rate of Oxidation of Chromium(III) in Dilute Uranyl Sulfate Solution in the Presence of Ruthenium	41
IV. LABORATORY CORROSION STUDIES	47
A. Stress-Corrosion Cracking	47
1. Stress-Corrosion Cracking in Boiling Uranyl Sulfate Solution	47
2. Stress-Corrosion Cracking in High-Temperature Chloride- Containing Water	52
(a) Effect of Heat and Surface Treatments	52
(b) Behavior of Cast Stainless Steel	55
3. Stress-Corrosion Cracking in Oxygenated Thorium Oxide Slurry	58

CONTENTS (cont'd.)

	<u>Page No.</u>
B. Chemiluminescent Solution for Detection of HRT Core Tank Defect	58
C. Miscellaneous Corrosion Tests	60
1. Multimet	60
2. Nitrided Titanium and Zircaloy-2	61
V. REFERENCES	66

I. SUMMARY

A simulated HRT fuel solution was unstable when passed through a heated Zircaloy-2 bypass section installed on a titanium loop. Losses of uranyl, cupric, and nickel sulfates were observed when the temperature of the solution emerging from the bypass was as low as 290°C. The solution was completely stable, however, when circulated isothermally at 320°C. Experiments are in progress to determine whether a second liquid or solid phase formed on the hot pipe wall.

The 0.04 *m* UO_2SO_4 solutions containing 0.025 *m* D_2SO_4 and 0.03 *m* CuSO_4 in heavy water were not completely stable at 300°C when either 0.04 *m* Na_2SO_4 or 0.04 *m* K_2SO_4 was added to the solution. In both cases about 30% of the copper was lost from solution. The only alkali or alkaline-earth sulfate which, when added to the uranyl sulfate solution, gave a stable solution less corrosive than the uranyl sulfate solution was magnesium sulfate.

The rate at which chromium(III) is oxidized to chromium(VI) in a ruthenium-containing uranyl sulfate solution has been measured at 225, 250, and 275°C. At 300°C the rate was too fast to be measured with the existing equipment.

The effect of cold work and heat treatment on type 347 stainless steel was investigated. The effect of cold work was not discernible. Treatment at 1950°F for 1 hr followed by a water quench produced a more corrosion-resistant condition than was present in the "as received" alloy.

Tests run in chloride-containing water at 200°C showed that both phosphate and fluoride ions partially inhibited stress-corrosion cracking of type 347 stainless steel, but neither was completely effective.

Stress-corrosion cracking of type 347 stainless steel occurs in most cases upon exposure to 0.04 m UO_2SO_4 -0.02 m H_2SO_4 -0.005 m $CuSO_4$ solution containing chloride ions at atmospheric boiling temperature. Recent tests have shown that the uranyl ion increases the effectiveness of the chloride ion. Other tests have shown that the concentration of uranyl sulfate is also important; cracks occurred when the solution contained 0.04 and 0.20 m UO_2SO_4 and 50 ppm chloride, but no cracking was observed in either more dilute or more concentrated solutions.

In chloride- and oxygen-containing water at 300°C, all type 347 stainless steel U-bend specimens developed cracks in 500 hr or less whether the surface had been electropolished, pickled, or had been left covered with a heavy oxide scale. Cracking also occurred even when the specimens were annealed after stressing. Pretreatment in high temperature, dilute chromate solutions was ineffective in preventing cracking. However, pretreatment in 100°C uranyl sulfate solutions apparently gave some protection against cracking on subsequent exposure of type 347 stainless steel to high-temperature chloride-containing water.

Cast type 347 stainless steel specimens have shown no susceptibility to cracking in either boiling 42% magnesium chloride or in high-temperature, chloride-containing water. Also, wrought type 347 stainless steel and Zircaloy-2 U-bend specimens have not cracked during exposure to oxygenated thorium slurries containing 100 ppm chloride at 300°C.

Tests were run with a Luminol solution to determine the applicability of chemiluminescence as a means of providing illumination where electrical illumination is difficult. With the proper concentration of reagents, the glow of the solution persists for more than an hour.

Corrosion tests with Multimet showed it to be more resistant (but not completely immune) to stress-corrosion cracking than type 347 stainless steel. In high-temperature uranyl sulfate solutions Multimet is only slightly less resistant to corrosion than type 347 stainless steel and should be suitable for certain reactor applications.

Specimens of nitrided titanium and Zircaloy-2 were subjected to test in a simulated fuel solution and in water at 300°C. In both environments the titanium specimens showed negligible attack, whereas Zircaloy-2 corroded at 14 mpy in each case. However, surface cracks were apparent in both materials before test, and on this basis it is doubtful that nitriding the surface of either titanium or Zircaloy-2 would produce a useful, hard surface.

II. INTRODUCTION

The data presented in the following pages represent the detailed results obtained during the past quarter (July 31, 1958, to October 31, 1958) by the Solution Materials Section of the Reactor Experimental Engineering

Division. A summary of the data has been given in the Homogeneous Reactor Project Quarterly Progress Report for the period ending October 31, 1958.

The data presented in this report are, for the most part, preliminary and the interpretation of the results may change as further experimentation is completed.

III. 100A LOOP PROGRAM (R. S. Greeley, S. E. Bolt, W. C. Ulrich, E. S. Snavely, N. E. Wisdom,* H. C. Savage, J. C. Griess)

A. Second-Phase Behavior of Dilute Uranyl Sulfate Solutions

In view of the possibility that second-liquid-phase separation could have occurred in localized regions of the HRT, a more extensive investigation of the second-phase behavior of dilute uranyl sulfate solutions than was described in the previous report¹ was warranted. The titanium loop used previously was fitted with an electrically heated 3/8-in. OD Zircaloy-2 bypass line through which solution could be circulated at 0.2 to 0.6 fps. Two valves were connected so that the solution in the Zircaloy-2 pipe could be isolated and sampled. Figure 1 shows a sketch of the assembly.

The solution circulated in the first test was similar to that in the HRT core system at low power during run 17; viz., 0.025 m UO_2SO_4 containing 0.014 m D_2SO_4 , 0.011 m $CuSO_4$, and 0.004 m $NiSO_4$ in heavy water. The solution was circulated in the main loop at 280°C while the bypass stream was increased to several higher temperatures. Figure 2 illustrates the changes in composition that occurred in samples of solution taken from the main loop.

*Summer employee

Fig. 1. Heated Zircaloy-2 Pipe Section

Fig. 2. Changes in Concentrations of Various Ions in Solution Circulated in Titanium Loop with Heated Zircaloy By-Pass.

When the outlet temperature of the bypass line was brought to 320°C with the pump on 20 cps (to give a flow rate of 0.2 fps through the bypass), uranium, copper and nickel sulfates were lost from the main circulating stream. The acid concentration decreased more slowly and to a lesser degree; and as a result, the acid-to-uranium ratio increased just as in the HRT at higher power.² However, no net increase in the amount of acid occurred, and in this regard the results did not agree with the HRT experience. The flow rate through the bypass was then increased to 0.6 fps by switching the pump to 60 cps. Within five minutes the uranium concentration in the main circulating stream increased from 2 to 4 g per liter; within 15 min all of the uranium, copper and nickel sulfates had been recovered.

Peculiarly enough, the acid concentration increased to above its original value as the uranium, copper, and nickel reappeared in the main stream. In previous tests with more concentrated solution (0.17 m UO_2SO_4) in the absence of copper and nickel, the acid concentration in the main stream (light phase) increased when the heavy second-liquid phase formed and decreased to its original value when the heavy liquid phase disappeared.³ Hence the behavior of the acid concentration in the present runs was not consistent with previous work.

Following a period of isothermal operation at 280°C to insure complete dissolution of all components of the solution, the above test was repeated with the outlet stream from the Zircaloy-2 bypass at 310°C and then twice at 300°C. As can be seen in Fig. 2, the results were

qualitatively the same as before with the outlet stream at 320°C, except at 300°C unexplained irregularities were noted in all curves. In each case the uranium concentration in the main stream dropped to about 2 or 3 g per liter. Then, when the pump was switched to 60 cps, all of the uranium reappeared.

Finally, most of the salts were caused to deposit in the bypass by heating the bypass stream to 300°C; the bypass was then valved off, cooled, and drained. The concentration of the drained solution was 245 g per liter uranium, 16.9 g per liter copper, 8.74 g per liter nickel, 155 g per liter sulfate, and 0.125 *m* D₂SO₄. Of course an unknown degree of dilution of the heavy phase by the light phase trapped between the valves occurred so that the actual concentration of heavy phase is unknown. The concentrations listed give molar ratios as follows: 12 UO₂SO₄ · 3 CuSO₄ · 2 NiSO₄ · 3 HSO₄⁻. The "missing" cations (or excess anions) are probably only an analytical error since the mole ratio of cations to anions is 0.96. If one accepts the analytical data for the bypass solution and considers the concentration of the original solution, the solution removed from the bypass was low in copper and acid relative to uranium.

The reason for the deposition of a second phase (solid or liquid) in the Zircaloy-2 bypass was not entirely clear. In an isothermal run at 320°C with the same solution in the same loop as in the above run, no components were lost from the solution in 50 hr of circulation. Therefore, either the wall temperature of the Zircaloy-2 bypass in the first test must have been greater than 320°C even when the solution outlet temperature

was as low as 300°C (with the main loop solution at 280°C); or else boiling of the solution at the Zircaloy-2 wall caused crystallization of salts on the wall.

A second test was made in order to see whether simple boiling of the solution flowing past the Zircaloy-2 wall would cause deposition. With the main stream at 250°C, the solution exiting from the Zircaloy-2 bypass at 287 to 290°C, flow rate through the bypass 0.2 fps (pump on 20 cps), and the system pressurized with oxygen to 1450 psia, deposition occurred. A calculation of the inside wall temperature of the Zircaloy-2 barrel indicated that the hottest temperature was about 325°C. Since this was above the boiling point at 1450 psia but below the second-liquid-phase temperature of the solution (334°C), it appeared that simple boiling caused the deposition. However, errors in the wall temperature calculation or in thermocouple readings could have occurred which would change this conclusion. In any case, lowering the temperature of the outlet stream 6° to 281°C caused reappearance of all species in the main circulating solution. Further experiments are in progress to determine the effect of gas or hydraulic pressurization and to determine more precisely conditions under which deposition of uranium in a heated bypass occurs.

The implications of these tests for the HRT are as follows: if the wall temperature in any location in the core region increased appreciably above the temperature of the bulk solution for any reason, deposition of a second phase (solid or liquid) could have occurred if the flow rate of solution past that location were a few tenths of a foot per second or less. If the location were in a region of high neutron flux, the second phase would heat up rapidly

due to the very high uranium concentration. The end result would be a region of high-temperature, high-uranium concentration and high-fission density, all of which would cause a high corrosion rate of the Zircaloy-2. Such a phenomenon appears to have occurred in the HRT.

B. Stability of Dilute Uranyl Sulfate Solutions Containing Alkali or Alkaline-Earth Sulfates

The previous report presented data on 0.04 m UO_2SO_4 solutions containing lithium, rubidium, beryllium, or magnesium sulfates in addition to 0.025 m D_2SO_4 and 0.03 m $CuSO_4$ in heavy water.⁴ More recently, data have been gathered on such solutions containing sodium and potassium sulfates. Table I is a list of the initial and final concentrations of the various ions in all of the runs made at 300°C.

None of the solutions containing the alkali-metal sulfates was completely stable. In the runs with the solution initially containing 0.04 m UO_2SO_4 + 0.025 m D_2SO_4 + 0.03 m $CuSO_4$ + 0.04 m added sulfate, the unstable species was mainly copper. However, solids which contained 3 to 15% uranium and smaller amounts of alkali metal (probably as the sulfate) were collected in the hydroclone underflow pot during every run. In run G-112 in which the copper concentration was lowered to 0.01 m , uranium became the main unstable species. In run G-110 in which 0.087 m Rb_2SO_4 and 0.004 m $NiSO_4$ were present originally in the solution, nearly half of the uranium and a third of the copper were lost. In run G-109 with only 0.021 m Rb_2SO_4 and no nickel, only a small amount of copper was lost.

Table I. Initial and Final Concentrations of Ions in Solution

Stability Runs in Heavy Water at 300°C (Molality)

Run No.	Length of Run (hr)		U (m)	Cu (m)	Ni (m)	Additive (m)	Acid (m)	Modified Marshall Ratio
G-108	130	Initial	.040	.028	<.001	Li ₂ SO ₄ .037	.026	.38
		Final	.040	.020	<.001	.037	.033	
G-111	117	Initial	.040	.027	<.001	Na ₂ SO ₄ .040	.026	.38
		Final	.040	.019	<.001	.038	.034	
G-112	200	Initial	.040	.010	<.001	Na ₂ SO ₄ .038	.028	.36
		Final	.035	.010	<.001	.038	.030	
G-113	200	Initial	.034	.024	<.001	K ₂ SO ₄ .030	.022	.38
		Final	.034	.016	<.001	.030	.028	
G-109	200	Initial	.038	.027	<.001	Rb ₂ SO ₄ .021	.025	.41
		Final	.038	.023	<.001	.021	.026	
G-110	182	Initial	.034	.0031	.004	Rb ₂ SO ₄ .087	.029	.34
		After 140 hr	.019	.0023	.001	.080	.046	
		Final*	.023	.0029	.001	.085	.050	
G-106	39	Initial	.040	.029	<.001	BeSO ₄ .039	.025	.56
		Final	.040	.029	<.001	.039	.025	
G-107	200	Initial	.036	.024	<.001	BeSO ₄ .033	.022	.55
		Final	.036	.024	<.001	.033	.022	
G-105	200	Initial	.040	.027	<.001	MgSO ₄ .034	.025	.50
		Final	.040	.026	<.001	.034	.029	

* Added acid after 140 hr.

The final column in Table I lists the Modified Marshall Ratio, defined previously⁴ as

$$\frac{1/2 U + Cu + Ni + M}{\sum \text{cations}}$$

where M is the alkali or alkaline-earth sulfate concentration and the sum of the cations includes the deuterium ion concentration as well as the uranium, copper, nickel and alkali or alkaline-earth metal ion concentrations. Interestingly enough, all of the alkali sulfate-containing solutions have ratios of 0.3 to 0.4, whereas the alkaline-earth sulfate-containing solutions have ratios of 0.5 to 0.6. Since a higher ratio would indicate a more stable solution, the alkaline-earth sulfate-containing solutions appear to be more stable than the alkali sulfate-containing solutions. Also, there appears to be little difference among the alkali metals except for cesium sulfate, which was not tested since the solution was unstable at room temperature. As noted previously,⁴ the magnesium sulfate-containing solution was the most promising both from a stability and a corrosion standpoint.

C. Stress-Corrosion Cracking Tests in Water at 200°C with Phosphate and Fluoride

In order to investigate the inhibition of stress-corrosion cracking more effectively than in previous tests,⁵ runs were made at 200°C rather than at 300°C. A control run with distilled water containing 50 to 60 ppm Cl⁻ as KCl was made in the system described before.⁶ Oxygen was bubbled through the feed solution so that the solution circulated at 200°C contained about 10 ppm oxygen. All of the type 347 stainless steel specimens, stressed beyond their yield strength, cracked in 200 hr, whether coupled to carbon steel or not. One unstressed specimen cracked at the bolt hole. Figure 3 is a representative photomicrograph of the stress-corrosion cracks observed. Cracks were so numerous that several specimens fell apart during handling. All cracks started from the tension side of the specimens. Stress-corrosion cracks were also found in the stainless steel loop proper.

The run was repeated twice; once with 60 ppm PO_4^{3-} as trisodium phosphate and once with 190 ppm F^- as potassium fluoride added to the chloride- and oxygen-containing water at 200°C. In the run with solution containing phosphate only one stress-corrosion crack was observed in the area of maximum applied stress on a type 347 stainless steel specimen. However, on two type 347 stainless steel specimens, stress-corrosion cracks were found in the region of the bolt hole drilled for mounting the specimen. Evidently a high residual stress was induced upon drilling the hole. A previous test⁵ at 300°C also showed that 60 ppm phosphate did not completely prevent cracking. In the run with the solution containing fluoride a few stress-corrosion cracks were found in the area of maximum applied stress on all type 347 stainless steel specimens. Figures 4 and 5 are representative photomicrographs of the cracks observed in the phosphate and fluoride-containing runs, respectively. As can be seen, the cracks were much smaller and less numerous than in Fig. 3.

Therefore, it was shown that phosphate and fluoride ions have an effect on chloride-induced stress-corrosion cracking of type 347 stainless steel. However, other runs must be made to determine whether complete prevention of cracking can be accomplished with higher concentrations or with combinations of these or other ions.

Corrosion rates of the carbon and stainless steel specimens are listed in Table II. The addition of phosphate to the chloride- and oxygen-containing water markedly decreased the corrosion of type 347 stainless steel and cut the corrosion rate of AISI type C-1016 carbon steel a factor of 2 to 3. The addition of fluoride to the water also decreased the corrosion of type 347 stainless steel markedly but reduced the corrosion rate of the carbon steel only slightly.

Fig. 3. Stress-Corrosion Cracks in Type 347 Stainless Steel
Stress Specimen Exposed 200 hr to Water Containing
50 ppm Cl and 10 ppm O₂ at 200°C

Fig. 4. Stress-Corrosion Cracks in Type 347 Stainless Steel
Stress Specimen Exposed 200 hr to Water Containing
50 ppm Cl, 60 ppm PO₄, and 10 ppm O₂ at 200°C

Fig. 5. Stress-Corrosion Cracks in Type 347 Stainless Steel
Stress Specimen Exposed 200 hr to Water Containing
50 ppm Cl, 190 ppm F, and 10 ppm O₂ at 200°C

Little effect of stress, galvanic coupling, or crevices was apparent on the general corrosion rates. The higher values for the corrosion rate of the uncoupled specimens were probably due to a larger area being available to the solution for attack since calculated corrosion rates were based on the same area for both coupled and uncoupled specimens. The coupled specimens were mounted one on top of the other so that solution was prevented from reaching a large part of the area in the crevice between the two specimens.

Table II. Corrosion Rates of Steels in Water Containing
50 ppm Chloride, 10 ppm Oxygen, and Phosphate
or Fluoride Additions at 200°C
(flow rate ~3 fps; totally immersed specimens)

Type Steel	Condition	Corrosion Rate, mpy		
		No Inhibitor	60 ppm PO ₄ ³⁻	190 ppm F ⁻
347 SS	Unstressed, uncoupled	-	0.8	-
	Stressed, uncoupled	15	0.8	0.7
	Stressed, coupled* to stainless steel	10	0.3	0.5
	Stressed, coupled* to carbon steel	8.1	0.7	0.6
	Unstressed, coupled* to carbon steel	8.9	0.7	0.3
AISI C-1016	Unstressed, uncoupled**	170	80	180
	Stressed, uncoupled**	230	78	150
	Stressed, coupled* to stainless steel	170	70	130
	Stressed, coupled* to carbon steel	150	52	83
	Unstressed, coupled* to carbon steel	120	56	-
	Unstressed, coupled* to stainless steel	150	72	100

* Also formed crevice with the coupled material.

** Except coupled to SS holder through bolts and fulcrum.

D. Effect of Cold Work and Heat Treatment on Corrosion of Type 347 Stainless Steel

Several previous investigations of the effect of metallurgical variables on corrosion of type 347 stainless steel have been made. These have shown that an anneal at 1950°F was beneficial but that a heat treatment at 2200 to 2300°F was deleterious.^{7,8} However, other variables, such as prior cold work, cooling rates, chemical composition, and annealing atmosphere were not completely controlled. Therefore, a further investigation was made in which the effects of cold work and subsequent heat treatment were observed on the corrosion of type 347 stainless steel.

A sufficient amount of 1/2-in. dia. type 347 stainless steel rod was obtained from a single heat of steel to provide material for all of the specimens desired. The chemical composition is listed in Table III. The material was received from the mill "hot rolled, annealed, and pickled" but was given a further one-hour anneal at 1950°F followed by a water quench at the Y-12 foundry. Various lengths of the 1/2-in. dia. rod were machined by centerless grinding to such diameters that subsequent cold swaging to 0.210-in. dia. gave 10, 25, 50, and 75% cold reduction in area. Finally, finished corrosion specimen pins were machined on a lathe from the swaged rods to give the required 0.203-in. dia. and 1.40-in. length. Control pins were machined directly from the 1/2-in. dia. rod.

Table III. Chemical Composition of Type 347 Stainless Steel
Used in Cold Work and Heat-Treatment Experiment

<u>Element</u>	<u>Weight Per Cent</u>
C	0.056
Cr	19.6
Ni	11.1
Mn	1.66
Cb	1.03
Ta	0.08
P	0.017
S	0.019
Si	0.86
Cu	0.18
Mo	0.12

One third of the pins were given no heat treatment. Another third was encapsulated in Vycor tubes under about 1 atm. helium, heated 1 hr at 1950°F, and water quenched. The final third was encapsulated as above, heated 2 1/2 hr at 2200°F, furnace-cooled to 1950°F, held 1 hr at 1950°F, and water quenched. All pins were then pickled* and electropolished.**

* Pickled 3 to 5 min in 50% HCl (inhibited); then 3 to 5 min. in 10% HNO₃ + 3% HF; 60°C in each case.

** Electropolished in acetic-perchloric acid mixture; no more than 10 mils removed from diameter.

The corrosion test consisted of a 200-hr exposure in 0.17 m UO_2SO_4 containing about 1000 ppm O_2 at 250°C. Duplicate pins of each degree of cold work and each heat treatment were exposed at 10, 13 and 17 fps. The velocities were chosen so as to expose the pins in the critical velocity region where differences would be most marked. Following exposure, all pins were scrubbed, defilmed, and weighed. Table IV summarizes the corrosion results.

It is apparent that the amount of cold work had no significant effect on the weight losses. On the other hand, as observed previously, subsequent heat treatment for 1 hr at 1950°F gave a marked decrease in the weight losses from pins that had not been heat treated. The heat treatment for 2 1/2 hr at 2200°F followed by 1 hr at 1950°F gave a slight decrease in weight loss. The deleterious effect previously observed was not found.

The photomicrographs of the specimens before corrosion testing are shown in Figures 6 through 20. At first glance the photomicrographs reveal no metallurgical reason for the results obtained. Certainly grain size, per se, had no effect on the corrosion rate, as appeared to be the case for type 304L stainless steel tested previously.⁷ Also, crystal deformation and extent of recrystallization appeared not to be controlling factors. It has been suggested that the large amount of impurities in ordinary type 347 stainless steel help to "anchor" the protective oxide film and so increase corrosion resistance.⁹ Figures 6 through 20 do not clearly support or deny this hypothesis. At any rate, the difference in microstructure and in corrosion rate between the specimens used in the current tests and

those used previously, both from material acceptable to HRP specifications, illustrates that minor chemical and metallurgical variables can have a major effect on subsequent behavior of the material.

Therefore, further metallurgical study must be made to determine, if possible, the controlling variables in the above corrosion results. Additional corrosion testing with specimens treated like those in Table IV is being carried out in boiling 65% nitric acid and in ferric sulfate solution.

Table IV. Weight Losses of Type 347 Stainless Steel
Pins in 0.17 m UO_2SO_4 During 200 hr at 250°C

All specimens were pickled and electropolished before testing and defilmed after testing.

Flow Rate, fps	Cold Reduction, %	Weight Loss, mg/cm^2			Average
		No Heat Treatment	1950°F 1 hr, Water Quenched	2200°F 2 1/2 hr 1950°F 1 hr, Water Quenched	
10	0	11.2	6.2	13.9	12.6
		21.2	7.6	15.4	
	10	19.6	7.7	12.9	13.0
			7.9	16.6	
	25	21.5	4.1	17.5	14.3
	50	33.4	5.3	13.5	13.7
		10.8	5.4		
	75	21.0	6.4	11.6	12.0
		<u>14.7</u>	<u>5.7</u>	<u>12.5</u>	
	Average	19.2	6.2	14.3	
13	0	33.1	9.0	15.1	24.3
		39.7	10.3	38.6	
	10	32.4	8.0	15.4	23.0
			10.6	48.7	
	25	36.4	6.5	22.9	21.9
	50	38.1	7.0	33.7	23.7
		37.7	7.9	17.8	
	75	28.7	7.1	21.8	19.6
		<u>34.5</u>	<u>6.2</u>		
	Average	35.1	8.2	26.7	
17	0	37.3	10.8	21.9	31.1
		41.8	33.3	40.9	
	10	39.3	9.0	35.3	27.5
			11.4	42.2	
	25	40.7	8.2	35.9	28.2
	50	40.7	6.9		24.3
		41.1	8.6		
	75	42.2	8.5	34.6	27.6
		<u>43.9</u>	<u>8.5</u>	<u>27.8</u>	
	Average	40.8	11.7	34.1

Longitudinal
250X

Transverse
250X

Fig. 6. Type 347 Stainless Steel, No Cold Work
(as received)

Longitudinal
250X

Transverse
250X

Fig. 7. Type 347 Stainless Steel, 10% Cold Worked

Longitudinal
250X

Transverse
250X

Fig. 8. Type 347 Stainless Steel, 25% Cold Worked

Longitudinal
250X

Transverse
250X

Fig. 9. Type 347 Stainless Steel, 50% Cold Worked

Longitudinal
250X

Transverse
250X

Fig. 10. Type 347 Stainless Steel, 75% Cold Worked

Longitudinal
250X

Transverse
250X

Fig. 11. Type 347 Stainless Steel, No Cold Work,
1 hr at 1950°F, Water Quenched

Longitudinal
250X

Transverse
250X

Fig. 12. Type 347 Stainless Steel, 10% Cold Worked,
1 hr at 1950°F, Water Quenched

Longitudinal
250X

Transverse
250X

Fig. 13. Type 347 Stainless Steel, 25% Cold Worked,
1 hr at 1950°F, Water Quenched

Longitudinal
250X

Transverse
250X

Fig. 14. Type 347 Stainless Steel, 50% Cold Worked,
1 hr at 1950°F, Water Quenched

Longitudinal
250X

Transverse
250X

Fig. 15. Type 347 Stainless Steel, 75% Cold Worked,
1 hr at 1950°F, Water Quenched

Longitudinal
250X

Transverse
250X

Fig. 16. Type 347 Stainless Steel, No Cold Work, 2 1/2 hr at 2200°F, Furnace Cooled to 1950°F, 1 hr at 1950°F, Water Quenched

Longitudinal
250X

Transverse
250X

Fig. 17. Type 347 Stainless Steel, 10% Cold Worked, 2 1/2 hr at 2200°F, Furnace Cooled to 1950°F, 1 hr at 1950°F, Water Quenched

Longitudinal
250X

Transverse
250X

Fig. 18. Type 347 Stainless Steel, 25% Cold Worked, 2 1/2 hr at 2200°F, Furnace Cooled to 1950°F, 1 hr at 1950°F, Water Quenched

Longitudinal
250X

Transverse
250X

Fig. 19. Type 347 Stainless Steel, 50% Cold Worked, 2 1/2 hr at 2200°F, Furnace Cooled to 1950°F, 1 hr at 1950°F, Water Quenched

Longitudinal
250X

Transverse
250X

Fig. 20. Type 347 Stainless Steel, 75% Cold Worked, 2 1/2 hr at 2200°F,
Furnace Cooled to 1950°F, 1 hr at 1950°F, Water Quenched

-14-

E. Rate of Oxidation of Chromium(III) in Dilute Uranyl Sulfate Solution in the Presence of Ruthenium

The marked acceleration of oxidation of chromium(III) to chromium(VI) in dilute uranyl sulfate solutions and in dilute sulfuric acid solutions containing ruthenium has been discussed.^{10,11} Since chromium(VI) is an excellent inhibitor of corrosion of stainless steel, the possibility exists that corrosion inhibition could be obtained in-pile if the ruthenium-catalyzed rate of production of chromium(VI) were greater than the radiation-induced reduction of chromium(VI). For this reason it was desirable to determine the ruthenium-catalyzed rate of production of chromium(VI) at several temperatures out of pile.

A solution of 0.04 *m* UO_2SO_4 containing 0.025 *m* H_2SO_4 was brought to temperature in a stainless steel loop and then chromic sulfate and ruthenium chloride were added to give 500 ppm Cr(III) and 25 ppm Ru(III) in solution. Samples of the solution were taken regularly for several days and analyzed for the various constituents. Runs were made at 225, 250, and 275°C (the oxidation of Cr(III) at 300°C was too rapid to measure). Figure 21 is a plot of $C_t - C_o$ versus time for all of the runs, where C_o is the chromium(VI) concentration when the chromic sulfate was added and C_t is the chromium(VI) concentration at time " t " hours later. Two runs were made at 250°C with slightly different amounts of chromium(III) and oxygen.

Fig. 21. Ruthenium Catalyzed Oxidation of Chromium (III) to Chromium (VI) in $0.04 \text{ m } UO_2SO_4 + 0.025 \text{ m } H_2SO_4 + 0.03 \text{ m } CuSO_4$.

As can be seen, the rate of formation of Cr(VI) was relatively rapid, even at 225°C. Kinetically, the results were different than expected. The rate of formation of Cr(VI) was found to depend on the reciprocal of the Cr(VI) concentration. This fact is brought out in Fig. 22, in which the rate ($d \text{ Cr(VI)}/dt$) is plotted against $1/\text{Cr(VI)}$. Excellent straight lines were obtained for each run. The difference between the two 250°C runs appeared to be due to a larger amount of Cr(III) being available in run I due to a previous run which left a large quantity of Cr_2O_3 in the loop.

The reason that the reaction rate at 250°C was more rapid than at 275°C appeared to be due to a difference in oxygen concentration. The oxygen concentrations just prior to adding the Cr(III) were 350 ppm in the 225°C run, 270 ppm in the 275°C run, and 1500 and 1460 ppm, respectively, in runs I and II at 250°C. If the slopes of the lines in Fig. 18 are divided by the oxygen concentration to the $3/2$ power and the resulting reaction rate constants plotted on semilogarithm paper versus the reciprocal of the absolute temperature, a straight-line relationship is obtained as shown in Fig. 23. Therefore, the following reaction rate equation is being followed:

$$\frac{d (\text{Cr VI})}{dt} = k \frac{(\text{O}_2)^{3/2}}{(\text{Cr VI})}$$

$k = 9.7 \times 10^{-4}$ at 225°C, 2.5×10^{-3} at 250°C, and 5.2×10^{-3} at 275°C, where the units of concentration are ppm and the unit of time is hr. The activation energy calculated from the slope of the line in Fig. 23 is 19 kilocalories per mole.

Fig. 22. Rate of Chromium (VI) Production vs. Reciprocal of Chromium (VI) Concentration.

UNCLASSIFIED
ORNL-LR-DWG 34497

Fig. 23. Reaction Rate Constant vs. Reciprocal Absolute Temperatures for the Ruthenium Catalyzed Oxidation of Chromium(III).

A dependence of the rate on the hydrogen ion activity would be expected also. However, the solution was partially buffered by the uranyl sulfate, copper sulfate, and sulfuric acid initially present so that little change in pH occurred during the run and the acid effect could be included in the rate constant, k .

A possible mechanism which fits the above equation is a heterogeneous one in which a chromic oxide surface site activated by ruthenium adsorbs either $3/2$ molecule oxygen or, more likely, 3 uranyl ions, and a surface oxidation reaction produces chromium(VI). The chromium(VI) then acts as a poison; i.e., is slowly desorbed. The uranyl ions, if they take part in the reaction, are reoxidized by $3/2$ molecules of oxygen. The chromic oxide is rapidly formed at 225 to 275°C from the Cr(III) added. The steps in the reaction then would be:

1. Precipitation of chromic oxide

2. Formation of active site (configuration unknown)

3. Adsorption of oxidant

4. Reaction

5. Desorption

6. Reoxidation of Uranyl Ions

Assumption of Langmuir-type adsorption isotherms for the $\text{Cr}_2\text{O}_7^{--}$ and the O_2 or UO_2^{++} gives the observed rate equation at constant pH if the $\text{Cr}_2\text{O}_7^{--}$ is strongly adsorbed.¹²

IV. LABORATORY CORROSION STUDIES (J. L. English, D. N. Hess, P. D. Neumann, J. C. Griess)

A. Stress-Corrosion Cracking

1. Stress-Corrosion Cracking in Boiling Uranyl Sulfate Solution

Stressed type 347 stainless steel is subject to cracking at the atmospheric boiling temperature in a simulated reactor fuel solution containing 0.04 m UO_2SO_4 , 0.02 m H_2SO_4 , 0.005 m CuSO_4 , and chloride concentrations ranging from 25 to 500 ppm.¹³⁻¹⁵ No cracking of the stainless alloy has ever been observed in a similar environment containing 0, 5, or 10 ppm of chloride. Metallographic examination of failed specimens has shown that cracking is predominantly transcrystalline.

Recently tests have been run to determine if the constituents in the fuel solution enhance the action of the chloride ion in producing cracking. Preliminary results of the tests have been reported.¹⁶

Elastically stressed type 347 stainless steel U-bend specimens prepared from annealed and pickled 0.025-in.- and 1/16-in.-thick sheet were used in the tests. (Each thickness was from a different heat of

steel.) In the boiling $0.04 \text{ } m \text{ } UO_2SO_4 - 0.02 \text{ } m \text{ } H_2SO_4 - 0.005 \text{ } m \text{ } CuSO_4$ solution containing 50 ppm of chloride, approximately 50% of a total of 60 specimens underwent cracking in 500 hr or less.

It should be noted that, of a total of nine specimens prepared from the 1/16-in.-thick stainless steel, all cracked during the first 200 hr of test. The 0.025-in.-thick specimens were less sensitive to cracking; approximately 40% (20 out of 51 specimens) cracked during the first 500 hr. Why the two different thicknesses showed different susceptibilities to cracking is not known.

Tables V and VI summarize the cracking behavior of the two heats of type 347 stainless steel in boiling solutions containing, either singly or in various combinations, the components in the simulated reactor fuel solution. All solutions contained 50 ppm of chloride. In a number of cases the tests were continued for as long as 2500 and 3000 hr, although cracking, when observed, occurred during the first 500 hr.

Several interesting observations resulted from the tests. In the case of the 0.025-in.-thick specimens, the only environment which produced cracking, other than the one with all components present, was the $0.04 \text{ } m \text{ } UO_2SO_4$ solution; three in a total of 16 specimens cracked. No cracking occurred in the $0.02 \text{ } m \text{ } H_2SO_4$ or $0.005 \text{ } m \text{ } CuSO_4$ solutions and, peculiarly enough, no cracking was observed in environments where the uranyl ion was present with either the sulfuric acid or the cupric sulfate.

Table V. Effect of HRT Fuel Solution Components on Stress-Corrosion
Cracking Behavior of 0.025-In.-Thick Type 347 Stainless Steel:
Atmospheric Boiling with 50 ppm Chloride

Solution	Number of Specimens	Total Time (hr)	Observations
0.04 m UO_2SO_4 0.02 m H_2SO_4 0.005 m CuSO_4	51	2500	20 specimens cracked in 500 hr or less
0.04 m UO_2SO_4 0.02 m H_2SO_4	8	2500-3000	No cracking
0.04 m UO_2SO_4 0.005 m CuSO_4	9	2500	No cracking
0.02 m H_2SO_4 0.005 m CuSO_4	9	2500	No cracking
0.04 m UO_2SO_4	16	2500-3000	3 specimens cracked in 500 hr or less
0.02 m H_2SO_4	8	2500-3000	No cracking
0.005 m CuSO_4	9	2500	No cracking

Table VI. Effect of HRT Fuel Solution Components on Stress-Corrosion

Cracking Behavior of 1/16-In.-Thick Type 347 Stainless Steel:

Atmospheric Boiling with 50 ppm Chloride

Solution	Number of Specimens	Total Time (hr)	Observations
0.04 m UO_2SO_4 0.02 m H_2SO_4 0.005 m CuSO_4	9	500	All specimens cracked in periods of 200 hr or less
0.04 m UO_2SO_4	6	500	All specimens cracked in periods of 200 hr or less
0.02 m H_2SO_4	6	2000-2500	One specimen cracked during interval between 200 and 500 hr
0.005 m CuSO_4	6	2000	No cracking

With the 1/16-in.-thick U-bend specimens, six out of six specimens cracked during the first 200 hr in the solution containing only uranyl sulfate and chloride ions. One isolated case of cracking occurred with a specimen exposed in chloride-containing 0.02 m H_2SO_4 solution; the other five specimens did not crack. Similarly, no cracking was experienced by specimens exposed in the chloride-containing 0.005 m $CuSO_4$ solution.

With the exception of the single case of cracking in the 0.02 m H_2SO_4 solution, the experimental data suggested that the uranyl ion increases the susceptibility of the type 347 stainless steel to stress-corrosion cracking in chloride environments. Accordingly, a series of boiling tests was run to determine the sensitivity to cracking as a function of uranium concentration. Uranyl sulfate concentrations of 0.004, 0.04, 0.20, 0.40, 1.33, and 2.26 m were examined. All solutions contained 50 ppm of chloride. U-bend stress specimens were prepared from the 0.025-in.-thick sheet. Triplicate specimens were run in each solution for 2500 hr. The results of the tests were: (1) cracking occurred in the 0.04 and 0.20 m UO_2SO_4 solutions during the first 500 hr and (2) no cracking was observed in the 0.004, 0.40, 1.33, and 2.26 m solutions. Thus it appears that there is an effect of uranium concentration on the incidence of cracking. It is planned to conduct a similar series of tests using specimens prepared from the 1/16-in.-thick heat of type 347 stainless steel which showed a higher susceptibility to cracking than did the 0.025-in.-thick sheet.

2. Stress-Corrosion Cracking in High-Temperature Chloride-Containing Water

(a) Effect of Surface and Heat Treatments

A number of tests in which type 347 stainless steel was exposed to chloride-containing distilled water with approximately 10 ppm of oxygen at 300°C has been run to determine the effect of various surface and heat treatments on the stress-corrosion cracking behavior of the alloy. Elastically stressed U-bend control specimens, prepared from 0.025-in.-thick mill-annealed and pickled sheet, developed cracks 100% of the time in the high-temperature water containing 100 ppm of chloride with an initial pH of 2.8. Cracking occurred during the first 500 hr of exposure, usually in the first 200 hr. The U-bend specimens were tested with sheared edges. No difference in the time to cracking in a similar environment was experienced when the specimens were annealed at 1950°F prior to bending to remove the sheared-edge effect. In one set of the tests, the specimens were pickled to remove the annealing scale; in a second set, specimens were exposed with the scale present. Regardless of the presence or absence of the scale, all specimens cracked during the first 200 hr. Specimens which were electropolished prior to forming exhibited a similar sensitivity to cracking in the chloride-containing environment.

In other tests in an environment containing 25 ppm of chloride and initial water pH of 10.5, specimens were first annealed in air at 1950°F both before and after cold-forming into U-bends. In each case the specimens were not pickled. The specimens that were cold-formed

after annealing underwent cracking during the first 300-hr exposure. The preliminary data for the specimens annealed after cold-forming and stressing indicated an increased resistance to cracking during 800- and 2000-hr tests. During these periods, no visible signs of cracking were observed by low-magnification examination. However, metallographic examinations of the specimens upon completion of the tests disclosed a number of transcrystalline cracks in all specimens such as are shown in Fig. 24.

Of pertinent interest was the fact that unstressed control specimens which were also annealed in air at 1950°F and exposed in the same environment were also subject to cracking as shown in Fig. 25.

In an effort to improve the resistance of type 347 stainless steel to cracking in high-temperature chloride-containing water, two chemical pretreatments were examined. One treatment consisted of exposing stressed U-bend specimens for 100 hr at 300°C in water containing 500 ppm of chromate as sodium chromate. The second treatment consisted of exposing stress specimens for 100 hr at atmospheric boiling in a simulated reactor fuel solution containing 0.04 m UO_2SO_4 , 0.02 m H_2SO_4 , and 0.005 m $CuSO_4$. The use of the reactor solution for prefilming type 347 stainless steel specimens stressed before prefilming has been found to be 100% effective for preventing cracking in the same boiling fuel solution containing 50 ppm of chloride.¹⁷

Fig. 24. Cracks in Type 347 Stainless Steel
Annealed after Cold Forming and Exposed
for 800 hr in Water Containing
25 ppm of Chloride at 300°C

Fig. 25. Cracks in Annealed and Unstressed
Type 347 Stainless Steel after 300-hr
Exposure in Water Containing
25 ppm Chloride at 300°C

The chromate-pretreated specimens were exposed at 300°C in water containing 100 ppm of chloride with an initial pH of 2.8. Cracking of all specimens took place in less than 100 hr. The uranyl sulfate-pretreated specimens were exposed at 300°C in water containing 25 ppm of chloride with an initial pH of 2.8. The specimens were resistant to cracking during the first 200 hr; however, during the interval between 200 and 300 hr, cracking did occur.

Thus, in summary, none of the various surface and heat treatments investigated as means for enhancing the stress-corrosion cracking resistance of type 347 stainless steel in high-temperature chloride-containing water has been effective in accomplishing this purpose. More and more, the experimental evidence indicates that the only positive method, other than by cathodic protection, for preventing the cracking of wrought type 347 stainless steel is by maintaining the chloride concentration at very low levels. Under certain conditions inhibitors may be partially effective, but they cannot be relied on under all conditions.

(b) Behavior of Cast Stainless Steel

Simple beam-type stress specimens were machined from 3-in. sch-80 centrifugally cast type 347 stainless steel pipe and were exposed in a stressed condition in a number of environments which were known to produce cracking in wrought austenitic stainless steels. The results of the tests appear in Table VII. No cracking has been

observed in any of the tests thus far. The boiling 42% MgCl_2 solution which produces cracking in wrought type 347 stainless steel in a matter of several hours failed to cause cracking of the cast alloy during a test period of 30 hr. Severe subsurface attack was produced, however, as shown in Fig. 26. Similarly, the high-temperature chloride-containing environment generally produces cracking of wrought type 347 stainless steel in shorter intervals than reported in Table VII.

Table VII. Stress-Corrosion Cracking Behavior of Cast
Type 347 Stainless Steel

Environment	Chloride Content (ppm)	Initial Solution pH	Temp. (°C)	Exposure Time (hr)	Remarks
42% MgCl_2			154	30	No cracking; sub- surface attack
Distilled H_2O^*	<0.5	6.5	300	800	No cracking
	100	2.8	300	200	No cracking
	100	6.5	300	400	No cracking
	100	6.5	300	1000	No cracking
	100	10.5	300	200	No cracking

* All tests at 300°C were made with approximately 10 ppm of oxygen.

Fig. 26. Subsurface Attack on Cast Type 347 Stainless Steel after 30 Hr in Boiling 42% MgCl_2 Solution

Studies with cast type 347 stainless steel are being continued. The preliminary experimental data show that the cast alloy is appreciably more resistant to stress-corrosion cracking in chloride-containing environments than is the wrought alloy. Actually, not a single incidence of cracking has been observed in tests with the former material thus far. In view of the indicated superiority of the cast alloy with regard to resistance to cracking, it should be the preferred choice over the wrought material in applications where it is feasible to use cast material.

3. Stress-Corrosion Cracking in Oxygenated Thorium Oxide Slurry

The stress-corrosion cracking behavior of Zircaloy-2 and type 347 stainless steel are undergoing examination at 300°C in air-saturated thorium oxide slurry with and without an added 100 ppm of chloride as sodium chloride. The chloride concentration was based on thoria content. The slurry was prepared from LO-37-1400 thorium oxide which contained 300 g of ThO_2 per 100 g of H_2O . The U-bend specimens were completely covered by the oxide during test.

The Zircaloy-2 specimens were relatively unaffected after 1000 hr in the chloride-free and the chloride-present tests. No cracking was observed. All specimens developed lustrous, adherent, and uniformly thin films.

In 600-hr tests in the absence of chloride, type 347 stainless steel stress specimens developed thin, straw-colored films. No cracking occurred. With chloride present, specimens developed heavy, dark-colored films; no cracks were found.

In the tests containing initially 100 ppm of chloride, analysis of the supernatant liquids after the first 100 hr of test showed the chloride concentrations to be less than 5 ppm. The tests are being continued.

B. Chemiluminescent Solution for Detection of HRT Core Tank Defect

Since the possibility existed that difficulties may be encountered in locating the defect in the Zircaloy-2 core tank of the HRT by examination with electrical illumination, a method of detection using chemiluminescence as

the light source was investigated. If used, the method would entail the introduction of the reagent into the empty core tank and observing from the blanket side the luminescent solution leaking through the defect. The chemiluminescent solution intended for the application was similar to the one described by Huntress et al.¹⁸

The solution consisted of a mixture of Luminol (5-amino-2, 3-dihydro-1, 4 phthalazinedione), hydrogen peroxide, potassium ferricyanide, and sodium hydroxide. Experiments were performed to produce the brightest and most long-lasting glow by varying the concentrations of the reagents. The sodium hydroxide concentration was the most important variable; it was found that the higher the sodium hydroxide concentration, the brighter the glow. However, under these conditions, the life of the glow was relatively short. The optimum conditions using heavy water as the solvent were: 15 ml of 5% NaOH solution were added to 1 g of Luminol in 1 liter of heavy water; to 750 ml of this solution 250 ml of 2.5% $K_3Fe(CN)_6$ and 20 ml of 3% H_2O_2 solution were added. The resulting solution had appreciable brightness for approximately 15 min, moderate brightness for 30 min, and ceased glowing after slightly more than 1 hr. It was observed that to obtain solutions of comparable brightness and longevity, the alkali requirement for the heavy water solutions was about 50% greater than that required for the light water solutions.

The defect in the HRT core vessel was recently located clearly with specially designed remote viewing equipment, and it was not necessary to resort to the use of the chemiluminescent solution. However, the method may prove useful in some future applications where it is desirable to locate a large leak which cannot be easily illuminated.

C. Miscellaneous Corrosion Tests

1. Multimet

Multimet, a product of the Haynes Stellite Company, has a nominal chemical composition of 20-22.5% Cr, 19-21% Ni, 0.08-0.16% C, 2.5-3.5% Mo, 0.75-1.25% Nb plus Ta, 2-3% W, 18.5-21% Co, 0.1-0.2% N, and balance iron. Because the alloy possesses excellent mechanical properties, it was considered as a possible bolt material for a number of HRT applications. A wide range in mechanical properties of the alloy can be developed by various forging operations. Heat treating at 2100 to 2300°F followed by rapid cooling after hot working greatly improves ductility and toughness, but decreases strength. Preliminary corrosion tests with heat-treated specimens of the alloy (23 Rockwell C) exposed in oxygenated $0.04\text{ }m\text{ }UO_2SO_4$ - $0.02\text{ }m\text{ }H_2SO_4$ - $0.005\text{ }m\text{ }CuSO_4$ solution at 300°C resulted in an observed corrosion rate of 1 mpy.¹⁹

In the present investigation, corrosion specimens were prepared from 0.094-in.-thick sheet which had been hot rolled to 0.098 in. followed by cold rolling to 0.094 in. from 1/4-in.-thick sheet. The specimens were annealed for 1 hr at 2200°F in a hydrogen atmosphere.

The specimens were exposed for 1000-hr periods in oxygenated $0.04\text{ }m\text{ }UO_2SO_4$ - $0.02\text{ }m\text{ }H_2SO_4$ - $0.005\text{ }m\text{ }CuSO_4$ solution at 100, 200, and 300°C. The observed corrosion rates were 0.2, 2, and 3 mpy, respectively. All specimens were subject to an acid-etch type attack which increased in severity with increased temperature. Annealed specimens were also exposed at atmospheric boiling in a 5% HNO_3 solution; the corrosion rates were less than 0.1 mpy.

The stress-corrosion cracking behavior of the alloy was examined in boiling (100°C) 0.04 m UO_2SO_4 -0.02 m H_2SO_4 -0.005 m CuSO_4 solution containing 50 ppm of chloride and in boiling 42% MgCl_2 solution. In the former solution, no cracking occurred during a test period of 2500 hr. A time of 40 hr was required to produce cracking in the magnesium chloride environment. Elastically stressed U-bend specimens were used in both tests.

Although the corrosion attack on Multimet by high-temperature uranyl sulfate solutions is somewhat greater than that experienced by type 347 stainless steel, its adequate corrosion resistance combined with its favorable mechanical properties warrant consideration of its use in certain reactor applications.

2. Nitrided Titanium and Zircaloy-2

The corrosion resistance of nitrided titanium-55A, titanium-75A, and Zircaloy-2 was determined at 300°C in deionized water and in oxygenated 0.04 m UO_2SO_4 -0.025 m H_2SO_4 -0.01 m CuSO_4 solution. The surface-hardening treatment on the test specimens was conducted for 16 hr at 1600°F in an atmosphere of nitrogen containing 0.1% oxygen by the HRP Metallurgy Group.²⁰ They found that the depth of hardening was greater with a small amount of oxygen present as compared to that obtained in a commercially pure nitrogen atmosphere. The surface hardness of the specimens was 550 DPH (ca 52 Rockwell C); at a depth of 3 mils, the hardness was 300 DPH (ca 30 Rockwell C). Grain growth and surface cracking occurred in the titanium specimens; a volume increase occurred in the Zircaloy-2 specimens.

A summary of corrosion data for 1000-hr tests appears in Table VIII. The titanium-75A and Zircaloy-2 specimens were in the form of pins; the individual titanium-55A specimens were obtained by quartering a $3/16 \times 1 \ 3/8 \times 1 \ 3/8$ -in. piece after nitriding. Consequently, each of the specimens had two faces of bare metal exposed.

Table VIII. Corrosion of Nitrided Titanium and Zircaloy-2
by Several Environments at 300°C

(Test Time: 1000 Hr)

Material	Corrosion Rate (mpy)	
	HRT Fuel Soln.*	Deionized H ₂ O
Titanium-55A	Gain	Gain
Titanium-75A	< 0.1	0.2
Zircaloy-2	14	14

* Oxygenated 0.04 m UO₂SO₄-0.025 m H₂SO₄-0.01 m CuSO₄ solution.

The titanium-55A specimens exhibited slight weight gains in both environments. The nitrided surfaces of the specimen exposed in the uranyl sulfate solution exhibited a variegated gold-and-blue-colored film; the surfaces of the water-exposed specimen were lustrous and gold colored.

The nitrided titanium-75A pins showed corrosion rates of less than 0.1 mpy and 0.2 mpy, respectively, in the uranyl sulfate and de-ionized water environments. Yellow-colored deposits were observed in imperfections on the surfaces of specimens in both environments. A photomicrograph of the cross-sectional area of the uranyl sulfate-exposed titanium-75A pin is shown in Fig. 27. Actually, a comparison of the microstructures of the exposed pin with an unexposed nitrided pin²⁰ failed to disclose any gross changes resulting from the corrosion test. Similar surface cracks as shown in Fig. 27 were found in the unexposed specimen. The cracking was attributed to brittleness in the grains as a result of high nitrogen and oxygen contents.

The Zircaloy-2 specimens underwent substantial attack by both the uranyl sulfate solution and the deionized water; the 1000-hr corrosion rate was 14 mpy in both solutions. Practically all the weight loss experienced by the specimens took place during the first 50 hr of exposure in each environment. The original heavily roughened gray-white colored surfaces of the two specimens underwent no apparent change as a result of the exposures. Figure 28 shows a low-magnification view of one end of the Zircaloy-2 specimen that was exposed in the uranyl sulfate solution. The gray-white color and the volume changes in the pin were produced by the nitriding process, not the corrosion-test exposure.

Figure 29 shows a longitudinal section of the same Zircaloy-2 specimen shown in Fig. 28. The pits, ranging to 6 mils in depth, were reported to contain zirconium oxide.²¹ Although similar pits (or cracks) were found in unexposed nitrided Zircaloy-2 specimens, it was felt that some increase in the depth of penetration by pitting was produced by the exposure.

Fig. 27. Transverse Section of Nitrided Titanium-75A Pin after
1000 Hr at 300°C in Oxygenated
0.04 m UO_2SO_4 -0.025 m H_2SO_4 -0.01 m CuSO_4 Solution
Etched in 8% HF-46% HNO_3 -46% H_2O

Fig. 28. End of Nitrided Zircaloy-2 Pin
after 1000 Hr at 300°C in Oxygenated
0.04 m UO_2SO_4 -0.025 m H_2SO_4 -0.01 m CuSO_4
Solution

Fig. 29. Longitudinal Section of Nitrided Zircaloy-2 Pin
after 1000 Hr at 300°C in Oxygenated
0.04 m UO_2SO_4 -0.025 m H_2SO_4 -0.01 m CuSO_4 Solution
Etched in 8% HF -46% HNO_3 -46% H_2O

It was concluded that on the basis of surface cracking experienced by titanium specimens during the nitriding process and on the volume changes incurred in Zircaloy-2 specimens by nitriding, that the nitriding process for increasing the surface hardness of the two materials does not offer much hope for practical applications.

V. REFERENCES

1. J. C. Griess et al., Quar. Rep. of the Solution Corrosion Group for the Period Ending July 31, 1958, ORNL CF-58-7-132, pp 16-18.
2. H. F. McDuffie, Chemical Indications of HRT Misbehavior in Run 17A, ORNL CF-58-9-41, p 3.
3. Reference 1, p 17.
4. Reference 1, pp 10-15.
5. Reference 1, pp 18-21.
6. J. C. Griess et al., Quar. Rep. of the Solution Corrosion Group for the Period Ending July 31, 1957, ORNL CF-57-7-121, p 7.
7. J. C. Griess et al., Quar. Rep. of the Solution Corrosion Group for the Period Ending April 30, 1956, ORNL CF-56-4-138, pp 24-28.
8. Reference 6, pp 22-24.
9. E. G. Bohlmann, private communication.
10. J. C. Griess et al., Quar. Rep. of the Solution Corrosion Group for the Period Ending April 30, 1958, ORNL CF-58-4-131, pp 28-30.
11. Reference 1, pp 21-23.
12. S. Glasstone, K. J. Laidler, and H. Eyring, The Theory of Rate Processes, McGraw-Hill, New York, 1941, pp 382-385.
13. J. C. Griess et al., HRP Quar. Prog. Rep. April 30, 1957, ORNL-2331, pp 90-91.
14. J. C. Griess et al., HRP Quar. Prog. Rep. Oct. 31, 1957, ORNL-2432, pp 82-83.
15. J. C. Griess et al., HRP Quar. Prog. Rep. Jan. 31, 1958, ORNL-2493, p 92.
16. Ibid., pp 92-93.
17. Reference 1, pp 24-27.
18. E. Huntress, L. Stanley, and A. Parker, J. Chem. Ed., II, 1934, pp 142-145.

19. Reference 6, pp 55-56.
20. F. W. Cooke, Preparation of Nitrided Titanium and Zircaloy-2 Corrosion Specimens, HRP MET-35, July 16, 1958.
21. T. M. Kegley, Jr., and T. I. Henson, memo to D. N. Hess, October 20, 1958.

DISTRIBUTION

1. HRP Director's Office
2. G. M. Adamson
3. T. A. Arehart
4. A. L. Bacarella
5. J. E. Baker
6. J. M. Baker
7. J. C. Banter
8. H. F. Bauman
9. S. E. Beall
10. A. M. Billings
11. E. G. Bohlmann
12. S. E. Bolt
13. E. S. Bomar
14. N. C. Bradley
15. J. C. Bresee
16. N. A. Brown
17. F. R. Bruce
18. D. R. Bruley
19. J. R. Buchanan
20. W. D. Burch
21. C. A. Burchsted
22. S. R. Buxton
23. G. H. Cartledge
24. R. H. Chapman
25. R. D. Cheverton
26. C. J. Claffey
27. H. C. Claiborne
28. C. W. Collins
29. E. L. Compere
30. F. W. Cooke
31. J. S. Culver
32. D. Davis (AEC, O.R.)
33. R. J. Davis
34. V. A. DeCarlo
35. J. R. Engel
36. J. L. English
37. L. L. Fairchild
38. H. L. Falkenberry
39. D. E. Ferguson
40. J. D. Flynn
41. D. F. Frech
42. C. H. Gabbard
43. W. R. Gall
44. E. H. Gift
45. T. H. Gladney
46. H. E. Goeller
47. R. S. Greeley
48. A. T. Gresky
49. J. C. Griess
50. J. D. Grimes
51. R. H. Guymon
52. P. A. Haas
53. J. P. Hammon
54. P. H. Harley
55. R. J. Harvey
56. P. N. Haubenreich
57. J. K. Hayes
58. J. Hernandez
59. D. N. Hess
60. J. W. Hill
61. E. C. Hise
62. J. P. Harvis
63. S. Jaye
64. G. H. Jenks
65. K. O. Johnson
66. D. T. Jones
67. S. I. Kaplan
68. P. R. Kasten
69. F. A. Knox
70. J. O. Kolb
71. R. B. Korsmeyer
72. U. Koskela
73. K. A. Kraus
74. N. A. Krohn
75. J. A. Lane
76. C. G. Lawson
77. R. E. Leuze
78. R. B. Lindauer
79. R. A. Lorenz
80. M. I. Lundin
81. R. N. Lyon
82. W. L. Marshall
83. T. H. Mauney
84. J. P. McBride
85. H. F. McDuffie
86. R. A. McNeas
87. J. R. McWherter
88. O. Menis
89. E. C. Miller
90. F. C. Moesel (AEC, Wash.)
91. R. L. Moore
92. C. S. Morgan
93. P. D. Neumann
94. A. R. Olsen
95. L. F. Parsly
96. R. L. Pearson
97. F. N. Peebles
98. M. L. Picklesimer
99. R. M. Pierce
100. R. G. Pitkin

101. B. E. Prince
102. L. R. Quarles
103. S. A. Reed
104. W. D. Reel
105. L. Rice
106. D. M. Richardson
107. G. W. Rivenbark
108. R. C. Robertson
109. J. N. Robinson
110. M. W. Rosenthal
111. H. C. Savage
112. W. F. Schaffer
113. R. E. Schappel
114. H. K. Search
115. C. L. Segaser
116. E. M. Shank
117. A. J. Shor
118. M. D. Silverman
119. M. J. Skinner
120. E. S. Snavelly, Jr.
121. I. Spiewak
122. R. W. Stoughton
123. J. C. Suddath
124. C. D. Susano
125. J. E. Sutherland
126. J. A. Swartout
127. E. H. Taylor
128. W. Terry
129. D. G. Thomas
130. P. F. Thomason
131. M. Tobias
132. D. S. Toomb
133. W. C. Ulrich
134. R. E. Unger
135. R. Van Winkle

136. E. Volk
137. D. W. Vroom
138. R. E. Wacker
139. F. J. Walter
140. K. S. Warren
141. B. H. Webster
142. H. O. Weerer
143. A. M. Weinberg
144. K. W. West
145. S. H. Wheeler
146. J. C. Wilson
147. J. F. Winesette
148. R. H. Winget
149. C. E. Winters
150. L. F. Woo
151. W. L. Wright
152. O. O. Yarbrow
153. W. C. Yee
154. F. C. Zapp
155. ORNL Document Reference
Library, Y-12
156-157. Central Research Library (2)
158-159. REED Library (2)
160. ORNL-RC
161-162. Laboratory Records (2)
163-169. Westinghouse - PAR (7)
170-184. AEC, TISE, Oak Ridge (15)
185-187. M. A. Golik - Westinghouse -
Bettis (3)