217
4-5

2090

ANCR-1033

UC-80

MASTER

CORROSION OF THERMOCOUPLE SHEATH
MATERIALS IN A PRESSURIZED WATER
REACTOR ENVIRONMENT

BY

J.D. Tkach and R.H. Meservey

Aerojet Nuclear Company

NATIONAL REACTOR TESTING STATION

Idaho Falls, Idaho — 83401

DATE PUBLISHED—FEBRUARY, 1972

PREPARED FOR THE

U. S. ATOMIC ENERGY COMMISSION

IDAHO OPERATIONS OFFICE UNDER CONTRACT AT(10-1)-1375

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

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.

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.95

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or 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.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or 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.

CORROSION OF THERMOCOUPLE SHEATH MATERIALS
IN A PRESSURIZED WATER REACTOR ENVIRONMENT

BY

J. D. Tkach and R. H. Meservey

AEROJET NUCLEAR COMPANY

Date Published - February 1972

PREPARED FOR THE U. S. ATOMIC ENERGY COMMISSION
IDAHO OPERATIONS OFFICE
UNDER CONTRACT NO. (10-1)-1375

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Reg

ACKNOWLEDGMENTS

B. R. Merkley fabricated most of the test specimens and conducted the autoclave tests. D. D. Keiser and J. C. Downey performed the metallurgical tests and analysis and provided much information about corrosion of the materials. The authors thank these people for their invaluable cooperation and efforts.

ABSTRACT

Environmental corrosion behavior is a critical information item in pressurized-water reactor (PWR) applications. The service lifetime of specialized instrumentation detectors is sometimes determined by the corrosive behavior of the detectors in their environments. Of special interest was the corrosive behavior of thermocouples in borated water at 650°F and 2500 psig, because this represented the design conditions of the Loss-of-Fluid Test (LOFT) reactor and of many other commercial power-generating PWR's.

The LOFT reactor specifically requires many temperature measurements of the Zircaloy-4 fuel pin cladding using thermocouples having a 2000-hour operating lifetime. Thus, candidate thermocouple sheaths were selected and corrosion tested, both individually and welded to Zircaloy. The tests were performed in an autoclave in static water having 2000 ppm boron and 1-10 ppm oxygen. Operating conditions were 650°F and 2500 psig. Total time of the test was 2500 hours.

Candidate thermocouple sheath materials for temperature measurements on Zircaloy were niobium-1% zirconium (Nb-1Zr), platinum, tantalum, titanium, and Zircaloy. These choices were based on weld compatibility with Zircaloy.

Both Nb-1Zr and tantalum had rapid corrosion rates; the oxides formed in the process tended to spall, causing a weight loss. The spalling was indicative of nonadherent oxides and the material loss rendered these two metals unsuitable for PWR applications.

Platinum exhibited no changes during the test. However, the platinum-to-Zircaloy welds contained intermetallics which exhibited accelerated corrosion rates, eventually causing the weldment to embrittle after approximately 1000 hours of testing.

Titanium also showed excellent corrosion resistance during the test. However, titanium-to-Zircaloy tungsten-inert gas (TIG) arc-welded specimens showed rapid corrosion in the welds. The TIG process caused extensive mixing of the base metals in the weldment, and the titanium-zirconium alloy thus formed had a much greater corrosion rate than either titanium or zirconium alone. Additional specimens were welded using a LASER welder in which the weld process was extremely rapid and intermixing of the base metals was inhibited. This technique produced titanium-to-Zircaloy weldments that had corrosion rates comparable to that of Zircaloy.

Based on the results of the long-term corrosion tests and on the weld metallurgy, titanium was recommended for use as a thermocouple sheath material when the thermocouples were to be welded to Zircaloy-clad fuel pins and tested in a PWR environment.

CONTENTS

ACKNOWLEDGMENTS	ii
ABSTRACT	iii
I. INTRODUCTION	1
II. TEST CONDITIONS, APPARATUS, AND EXPERIMENTAL PROCEDURE	3
1. TEST CONDITIONS	3
1.1 Temperature	3
1.2 Pressure	3
1.3 Water Chemistry	3
1.4 Time	3
2. APPARATUS	4
2.1 Autoclave	4
2.2 Other Test Equipment	4
3. EXPERIMENTAL PROCEDURE	4
3.1 Sample Preparation	4
3.2 Test Procedure	5
3.3 Post-Test Examination	5
III. RESULTS AND DISCUSSION	6
1. CORROSION WEIGHT GAIN	6
2. EXAMINATION OF CORROSION	8
2.1 Zircaloy	8
2.2 Platinum	8
2.3 Titanium	15
2.4 Tantalum	21
2.5 Niobium-1% Zirconium	25
IV. CONCLUSIONS	27
V. REFERENCES	28
VI. BIBLIOGRAPHY	30

FIGURES

1. Corrosion weight gain curves for thermocouple sheath materials in 650°F, 2500 psi borated water	6

2. Platinum-13% rhodium-sheathed thermocouple TIG welded to Zircaloy	9
3. Platinum-13% rhodium-sheathed thermocouple TIG welded to Zircaloy	9
4. Platinum-13% rhodium-sheathed thermocouple TIG welded to Zircaloy	10
5. Platinum-13% rhodium TIG weldment remaining after thermocouple detached from the Zircaloy at the end of 2500 hours	11
6. Platinum-13% rhodium-sheathed thermocouple TIG welded to Zircaloy	11
7. Platinum-13% rhodium-sheathed thermocouple of Figure 6	12
8. Platinum wire LASER welded to Zircaloy.....	13
9. Platinum wire LASER weldment on Zircaloy	13
10. Platinum wire LASER welded to Zircaloy	14
11. Platinum wire LASER welded to Zircaloy	14
12. Platinum wire LASER weldment on Zircaloy	15
13. Titanium foil TIG welded to Zircaloy	16
14. Titanium foil TIG welded to Zircaloy	16
15. Titanium foil TIG welded to Zircaloy	17
16. Titanium foil TIG welded to Zircaloy	17
17. Titanium foil TIG welded to Zircaloy	18
18. Titanium foil TIG welded to Zircaloy and tested for 2000 hours	19
19. Titanium tubing LASER welded to Zircaloy	19
20. Titanium tubing LASER welded to Zircaloy	20
21. Titanium tubing LASER welded to Zircaloy	20
22. Tantalum corrosion coupon after 2500 hours of testing	21
23. Cross section of tantalum corrosion coupon of Figure 22	22
24. Tantalum foil TIG welded to Zircaloy	22
25. Tantalum foil TIG welded to Zircaloy	23

26. Tantalum foil TIG welded to Zircaloy	24
27. Tantalum foil TIG welded to Zircaloy	24
28. Niobium-1% zirconium corrosion specimen tested for 2500 hours	25
29. Niobium-1% zirconium-sheathed thermocouples tested for 500 hours	26

TABLES

I. Pilling-Bedworth Ratios of Metals Tested	8

CORROSION OF THERMOCOUPLE SHEATH MATERIALS IN A PRESSURIZED-WATER REACTOR ENVIRONMENT

I. INTRODUCTION

The high-temperature, high-pressure water used as a coolant in a modern pressurized-water reactor (PWR) presents a highly corrosive environment to many materials[1]. Although the free oxygen content of the water is maintained at a level of about 0.1 ppm, severe corrosion of many materials does occur. A complicating factor in the corrosion of materials in a PWR environment is the addition of boron and lithium to the coolant. Boron is added as a nuclear control agent and lithium is added as a pH control agent. The boron content is normally maintained in the range of 0 to 4000 ppm and the lithium in the range 0.1 to 3.0 ppm. While a considerable amount of corrosion data exists for materials exposed to 650°F, 2500 psig water, very little is available in which known boron, lithium, and oxygen levels were maintained.

Of special interest is the corrosive effect of the PWR environment on thermocouple sheath materials which will be used in the Loss-of-Fluid Test (LOFT) program. These thermocouples are to be attached to the Zircaloy-4 cladding of the LOFT fuel pins and will be used to measure core temperatures during the series of blowdown tests planned for this reactor. The LOFT tests are expected to produce fuel pin cladding temperatures as high as 2800°F. Thermocouples have been attached to Zircaloy-clad fuel pins previously, but the attachment was accomplished with an 1850°F braze, which essentially limited the measurement capability of those thermocouples[2,3]. Temperatures above the remelt temperature of this braze would cause disattachment of a thermocouple. Also, brazing to Zircaloy at 1850°F caused very large areas of complete annealing and recrystallization of the cladding; all of the cold-work properties of the cladding were lost when exposed to a brazing cycle.

Thus, the high temperatures involved and the desire to minimize heat-affected regions at points of thermocouple attachments dictated the following:

- (1) Welding, not brazing, must be used to attach thermocouples to the cladding.
- (2) The thermocouples must be metallurgically compatible with the Zircaloy in order to be welded to it.

Attachment of the thermocouple sheath material to the Zircaloy-4 fuel pin cladding presents some rather severe welding problems. Only a limited number of materials are suitable for use as small-diameter thermocouple sheaths that can be successfully welded to Zircaloy. Of the materials available, five were selected as candidates for the long-term corrosion tests. Selection was based on weldability to Zircaloy and availability as small-diameter thermocouple sheath material. Following is a brief discussion of the merits and demerits of each of the five materials.

- (1) Zircaloy. Excellent weld compatibility with itself. Excellent corrosion resistance in a high-temperature water environment. Vendors were uncertain about producing small-diameter, thin-walled Zircaloy tubing in the 24-foot lengths required for the LOFT application.
- (2) Platinum. Good weld compatibility with Zircaloy. Excellent corrosion resistance in a high-temperature water environment. Readily available as a thermocouple sheath.
- (3) Titanium. Excellent weld compatibility with Zircaloy. Vendors were uncertain about producing small-diameter titanium-sheathed thermocouples in the 24-foot lengths required for the LOFT application.
- (4) Tantalum. Good weld compatibility with Zircaloy. Readily available as a thermocouple sheath.
- (5) Niobium-1% zirconium. Good weld compatibility with Zircaloy. Some questions existed about producing 24-foot Nb-1Zr-sheathed thermocouples.

Specimens made from each of the above materials were prepared and tested. An autoclave in which the water chemistry was controlled to simulate that of the LOFT reactor coolant was used as a test vessel. The autoclave was operated continuously at 650°F and 2500 psig for 500-hour periods. Analysis of specimens was performed at the end of each 500-hour test interval. Testing was continued until a total of 2500 hours was accumulated.

II. TEST CONDITIONS, APPARATUS, AND EXPERIMENTAL PROCEDURE

1. TEST CONDITIONS

1.1 Temperature

Test conditions were maintained by controlling the autoclave temperature. Automatic control circuitry was used to maintain the water temperature at $650 \pm 6^\circ\text{F}$.

1.2 Pressure

Pressure in the autoclave vessel was 2500 ± 250 psig as a liquid-filled system.

1.3 Water Chemistry

Chemistry of the water was established by adding appropriate amounts of certain materials to distilled water prior to filling the autoclave vessel. The materials were added to simulate the "mid-range" chemistry of the LOFT reactor coolant water. Following is a list of the chemicals added and their concentrations:

- (1) Boron. 2000 to 2500 ppm added as boric acid (H_3BO_3).
- (2) Lithium. 1 to 2 ppm added as hydrated lithium hydroxide ($\text{LiOH}\cdot\text{H}_2\text{O}$).
- (3) Oxygen. 1 to 10 ppm. This concentration was obtained by bubbling oxygen through the water for a short period of time.
- (4) Chlorine. As a matter of interest the concentration of chlorine in the water was checked and found to be in the range 0.10 to 0.15 ppm.

1.4 Time

The autoclave was operated continuously for 500-hour intervals. At the end of each 500-hour interval the samples were removed and examined for corrosion products. Samples which were to be returned to the autoclave for further testing were recleaned prior to each 500-hour series. The test was continued until a total exposure time of 2500 hours was accumulated by the specimens.

2. APPARATUS

2.1 Autoclave

The autoclave used for this test had a one-gallon capacity vessel. The vessel had a five-inch inside diameter and was 12 inches deep. The vessel head contained a thermowell which placed a standard thermocouple near the geometrical center of the vessel. The output from this thermocouple was fed to an automatic control system to control power to the autoclave heaters and, hence, to control the operating parameters of the autoclave.

The autoclave was designed for operation at 650°F and 5000 psig. The tests were conducted in such a manner that liquid-full conditions were maintained when operating at the LOFT design conditions of 650°F and 2500 psig.

2.2 Other Test Equipment

- (1) Water Chemistry Tests. Water samples were drawn from the autoclave immediately prior to sealing and beginning the heatup. Samples were taken both in evacuated steel bombs and in sealed glass flasks for comparison. Oxygen analysis was done using both mass spectrometry and chemical titration techniques. After it was determined that the two techniques produced similar results, the titration technique was used exclusively for expedience. Titration techniques were also used for the boron and lithium analyses.
- (2) Weight Gain and Metallography. The weight of each specimen was recorded prior to testing and also at the end of its testing interval. A conventional laboratory analytic balance having an accuracy of ± 0.2 mg was used for sample weighing. Metallography of the corrosion specimens was performed using standard metallographic techniques. The specimens were cut and polished, and then bright field and polarized light photomicrographs were made.

3. EXPERIMENTAL PROCEDURE

3.1 Sample Preparation

In most cases corrosion specimens were made by cutting small strips of material from sheet stock. The strips were approximately one inch long and one-half inch wide. Thickness varied with the availability of material but was nominally 0.040 inch. These samples were tested both individually and welded to Zircaloy. The purpose of the welded specimens was to investigate the corrosion properties of the weld regions. The Zircaloy to which the specimens were welded was in the form of reactor-grade Zircaloy-4 tubing having a diameter of about 0.4 inch and a wall thickness of 0.025 inch. The Zircaloy was in a clean, bright condition and did not have a prior corrosion layer such as is sometimes used for fuel pins. Both tungsten-inert gas (TIG)

and LASER welding techniques were used to attach the specimens to the Zircaloy. Enough specimens of each type were prepared so that three could be removed for destructive analysis at each 500-hour interval and still leave enough specimens for the full 2500-hour test duration. Each specimen was assigned an identification number which was engraved in the specimen surface prior to testing.

3.2 Test Procedure

After being cut and marked for identification, the specimens were washed in alcohol. This was followed by weighing the individual specimens and recording these data in a logbook. The specimens were then placed in the autoclave vessel in preparation for 500-hour phases of continuous operation at pressure and temperature.

After preparing the autoclave water, the vessel was filled to capacity. During heatup, the excess water was manually vented to maintain the pressure at 2500 psig. After reaching a temperature of 650°F, all valves were closed and the autoclave was placed on automatic control.

At the end of 500 hours of operating the autoclave was shut down, and after cooling to room temperature, the specimens were removed. Appropriate specimens were chosen for analysis at this time. The remaining specimens were replaced in the autoclave for another 500-hour test phase. This process was repeated until a total of 2500 hours of exposure time was accumulated.

3.3 Post-Test Examination

As previously mentioned, all corrosion specimens were examined at the conclusion of each 500-hour test phase. Visual examination was performed as the specimens were removed from the autoclave. Any abnormal appearance was noted in the logbook. After allowing the specimens to become thoroughly dry, those chosen for sampling were weighed. A specimen was removed from any group of identical specimens which showed excessive corrosion; metallography was performed on the corrosion area to determine the extent of the attack. Photomicrographs were made of all regions of interest.

III. RESULTS AND DISCUSSION

1. CORROSION WEIGHT GAIN

Relative corrosion weight gains of the five candidate thermocouple sheath materials are shown in Figure 1. It was assumed that the weight gain experienced by a metal was due to uniform surface oxidation as shown by the general metal-water reaction equation

where M designates a metal and MO designates the oxide phase of that metal which forms at 650°F.

Fig. 1 Corrosion weight gain curves for thermocouple sheath materials in 650°F, 2500 psi borated water.

The weight gain curve for Zircaloy agreed well with published curves obtained using pure water[4,5] and chemically treated water[6]. Thus, the presence of the boron, lithium, and excess oxygen had not seriously affected the corrosion behavior of the Zircaloy in these tests[7]. It was therefore assumed that the water impurities also had no serious effect on the corrosion behavior of the other metals.

It was seen that titanium gained corrosion weight at approximately one-third the rate of Zircaloy, suggesting that it was very corrosion resistant. It was known that Zircaloy exhibited a corrosion "breakaway" phenomenon in which the weight gain curve suddenly experienced an increase in slope. This occurred after about 3500 hours of exposure at 650°F[4,5,8]. Breakaway was not observed with titanium in these tests, although it might occur beyond 2500 hours of testing.

No weight gain was observed with platinum.

Tantalum experienced a much more rapid oxidation rate than the Zircaloy. The resultant oxide was slightly nonadherent and tended to crack and split away from the base metal. This loss of material produced the negative slope in the weight gain curve. The dashed line is an extrapolation of the initial 500-hour corrosion rate and represents the expected weight gain curve for tantalum assuming that no material loss occurs. The material loss rendered tantalum unsuitable as a thermocouple sheath material in a PWR.

Niobium-1% zirconium experienced an extremely rapid oxidation rate. The resultant oxide was nonadherent and spalled from the base metal in relatively large amounts. The material loss was very large; about 1000 mg/dm² weight loss occurred after 2500 hours of testing. The curve in Figure 1 was inferred from the 500-hour weight gain data and from previous work that had been done[9]. The material loss rendered Nb-1Zr unsuitable as a thermocouple sheath material in a PWR.

The Pilling-Bedworth ratio (the ratio of the volumes of metal oxide to metal) indicates the general protective nature of a metal oxide. A ratio of one usually indicates a very protective oxide layer, while a ratio greater than one usually indicates a nonprotective, nonadherent layer. The larger the ratio, the less protective the oxide layer becomes. A large ratio suggests that the oxide formation experiences rapid growth, so it cracks and spalls from the base metal, exposing new metal for oxidation[10,11]. Pilling-Bedworth ratios for the metals tested are given in Table I in order of increasing value (generally decreasing protectiveness). A correlation of this table and the curves in Figure 1 substantiates the general validity of the Pilling-Bedworth ratio as a measure of oxide protectiveness. The correlation does not occur for titanium and Zircaloy; however, the Pilling-Bedworth ratio is not given for Zircaloy but for zirconium. The alloying additions in Zircaloy might cause its Pilling-Bedworth ratio to lie between those of titanium and tantalum.

TABLE I
PILLING-BEDWORTH RATIOS OF METALS TESTED^[9,10,11]

<u>Metal</u>	<u>Pilling-Bedworth Ratio</u>
Platinum	No oxide formation
Zirconium	~ 1.56
Titanium	1.73 - 1.95
Tantalum	2.33 - 2.54
Niobium	2.49 - 2.61

2. EXAMINATION OF CORROSION

2.1 Zircaloy

In all cases, the corrosion product on the Zircaloy was lustrous and black in appearance. It was very thin and adherent, as was expected[4,5]. The thickness of the oxide layer was estimated to be about 10^{-4} inches at the end of 2500 hours, based on a conversion factor that 385 mg/dm² weight gain was equivalent to a 0.001-inch thick oxide layer[6].

Zircaloy welds were not specifically investigated in this test. Much information concerning this type of weld was already available from many sources; the wide use of Zircaloy as fuel pin cladding in PWR's attested to its suitable properties in high-temperature water.

Because of the cold-working properties of Zircaloy, all tubing vendors contacted expressed doubts that Zircaloy could be manufactured in the small tubing sizes required for thermocouple sheathing.

2.2 Platinum

Platinum did not experience any observable changes during the test. The platinum-Zircaloy weldment, however, was known to contain intermetallic compounds which were inherently brittle. These compounds apparently also were highly susceptible to high-temperature water corrosion. The combination of this corrosion, and possibly a time-dependent phase change which led to separation of platinum and zirconium, caused failures in some welds[12]. For example, Figure 2 shows a platinum-13% rhodium (Pt-13Rh)-sheathed thermocouple TIG welded to Zircaloy. (Platinum-sheathed thermocouples were not available when these specimens were fabricated; Pt-13Rh-sheathed material was used instead. It was contended that for this test, Pt-13Rh would behave similarly enough to platinum that general corrosion behavior for platinum-Zircaloy welds could be deduced.) The actual weld area on this specimen was hidden beneath the rounded tip, as seen in the sectioned view of Figure 3.

7.8X Specimen 1-1

Fig. 2 Platinum-13% rhodium-sheathed thermocouple TIG welded to Zircaloy. This specimen was untested.

50X Specimen 1-1

Polarized Light

Fig. 3 Platinum-13% rhodium-sheathed thermocouple TIG welded to Zircaloy. This specimen was untested.

A very definite weld interface is seen in this dissimilar-metals joint. The size of the weldment on this type of specimen was typically 0.05 inch in diameter. This was a 0.040-inch diameter thermocouple and represented a typical size that might be used in LOFT.

After 2000 hours of testing, gross weld failures began to occur. A few welds failed while the specimens were in the autoclave. Figure 4 shows an axial cross section of such a specimen. It exhibits a zirconium-rich weldment that typically remained attached to the platinum; a crater was usually left in the Zircaloy. That is, the weldment usually became unattached at the weldment-Zircaloy interface. The wall of the Zircaloy tubing is shown for comparison.

50X Specimen 1-15

Polarized Light

Fig. 4 Platinum-13% rhodium-sheathed thermocouple TIG welded to Zircaloy. The thermocouple detached from the Zircaloy at the end of 2000 hours of testing. The actual region of attachment to the Zircaloy is not seen here.

It exhibits a large grain structure as a result of the TIG welding performed in that region. Figures 5 and 6 show thermocouple attachments that have and have not become detached, respectively, at the end of 2500 hours of testing. A thermocouple such as that in Figure 6 was pried off the Zircaloy quite easily after the test; the entire weldment (part of which can be seen at the tip of the thermocouple in Figure 6) was brittle. It is seen in cross section in Figure 7; the front portion of the weldment has a large darkened region that was not evident in untested specimens. This weld embrittlement was actually detected as early as 1000 hours of testing. The Zircaloy also showed a small

7.8X Specimen 1-16

Fig. 5 Platinum-13% rhodium TIG weldment remaining after thermocouple detached from the Zircaloy at the end of 2500 hours.

7.8X Specimen 1-18

Fig. 6 Platinum-13% rhodium-sheathed thermocouple TIG welded to Zircaloy. It remained attached after 2500 hours.

50X Specimen 1-18

Polarized Light

Fig. 7 Platinum-13% rhodium-sheathed thermocouple of Figure 6. Note the large grain structure in the Zircaloy.

circular region of white corrosion product around each weld area. This was probably a result of weld contamination that corroded preferentially.

Platinum wires simulating platinum-sheathed thermocouples were LASER welded to Zircaloy using a pulsed ruby LASER welder with a 0.010-inch diameter beam. All welding was done using an argon purge in the weld region. A typical welded specimen is shown in Figure 8. A series of overlapping welds can be seen around the tip of the wire.

Failures began to occur in these LASER welds as early as 500 hours. The wire usually fell from the Zircaloy, leaving a horseshoe-shaped series of craters as shown in Figure 9. There was no correlation between failures and exposure time; the random nature of this corrosion behavior rendered the LASER-welded platinum unsuitable for this application even for 500 hours.

An unexpected phenomenon occurred with these platinum-Zircaloy LASER welds. Figure 9 shows whitish microcracks emanating radially from the weld region. The general weld region had also bulged outward several thousandths of an inch. This occurred within the region defined by the light circular area around the weld. Again, there was no correlation between this occurrence and weld failures. For example, Figures 10 and 11 show sections of the weld regions of specimens that exhibited cracking after 500 hours and 1000 hours, respectively. The cracking was obviously very extensive. The wire in Figure 10 detached from the Zircaloy (500 hours), while that in Figure 11 had not detached (1000 hours). Figure 12 shows a similar section of a 2000-hour specimen; the platinum became detached from the Zircaloy but had not exhibited cracking in the weld. The cause of this behavior could have been a "cracking agent" present in the alloy of the weld[13]. No such cracks were

7.8X Specimen 10-2

Fig. 8 Platinum wire LASER welded to Zircaloy. This specimen was not tested.

7.8X Specimen 10-18

Fig. 9 Platinum wire LASER weldment on Zircaloy. The wire had detached after 2500 hours.

50X Specimen 10-15

Polarized Light

Fig. 10 Platinum wire LASER welded to Zircaloy. After 500 hours, cracking was observed at the welds, and the wire detached from the Zircaloy.

50X Specimen 10-17

Polarized Light

Fig. 11 Platinum wire LASER welded to Zircaloy. After 1000 hours, cracking was observed, but the wire remained attached.

50X Specimen 10-9

Polarized Light

Fig. 12 Platinum wire LASER weldment on Zircaloy. After 2000 hours the wire became detached from the Zircaloy. However, cracking was not seen. (This section was taken axially to the Zircaloy tubing, not transversely, as were the other figures. Thus, the curvature in the Zircaloy is not seen here.)

observed in untested specimens, so it is likely that the high-temperature water activated the phenomenon. No attempt was made to discover the cause of the cracking; rather, the purpose of the test was to investigate gross effects of the corrosive environment.

2.3 Titanium

As mentioned previously, titanium exhibited excellent corrosion resistance in the high-temperature water. The titanium corrosion coupons were initially clean and bright. As the test progressed, the color of the titanium changed to bright blue, then to purple, then to various gray shades of red or blue. The blue color was indicative of the titanium dioxide (TiO_2) phase[14]. No information concerning the temper of the titanium was available.

The titanium-zirconium binary phase diagram showed complete solid solubility for all compositions[15]. This suggested good weld compatibility between titanium and Zircaloy. Specimens were fabricated by TIG welding 0.006-inch-thick titanium foils to Zircaloy tubing; a typical weldment is shown in Figure 13. This weld is shown sectioned in Figure 14; a definite interface is seen in the dissimilar-metals joint.

In general, the weld areas showed slightly more corrosion than did the Zircaloy. In a few isolated cases, however, the welds showed extremely rapid corrosion. Figure 15, for example, shows a lateral section of a TIG-welded area that underwent 1000 hours of testing. A slight material loss was seen in this specimen. However, Figures 16 and 17 (2000 hours of testing) show a great amount of material loss. In fact, almost all of the weldment had spalled from

7.8X Specimen 15-1

Fig. 13 Titanium foil TIG welded to Zircaloy. This specimen was untested.

50X Specimen 15-1 Bright Field

Fig. 14 Titanium foil TIG welded to Zircaloy. This specimen was untested.

50X Specimen 15-3

Polarized Light

Fig. 15 Titanium foil TIG welded to Zircaloy. This specimen underwent 1000 hours of testing. Loss of material appears to be evident at the left-hand side of the weld. The actual weld (previously molten material) appears as the dark area of the foil. Notice the extremely large grains in the Zircaloy due to heating by the TIG welding process.

11X Specimen 15-5

Fig. 16 Titanium foil TIG welded to Zircaloy. This specimen underwent 2000 hours of testing. A large amount of material was lost from the weldment.

32X Specimen 15-5

Polarized Light

Fig. 17 Titanium foil TIG welded to Zircaloy. This specimen underwent 2000 hours of testing. Almost all of the weldment had spalled from the base metal. The dashed lines indicate the original surfaces.

the base metal. Notice that the weldment in Figure 17 penetrated the Zircaloy deeper than that in Figure 15. This suggested that intermixing and heat input in Figure 17 was much more extensive than that in Figure 15. A literature source suggested that the alloy, titanium-50% zirconium, would be much more susceptible to corrosion than any other composition of the titanium-zirconium system[16]. It was possible that extensive intermixing (occurring randomly during the welding) could have been the cause of the random corrosion seen in these specimens. Figure 18 shows another specimen after 2000 hours of testing. Compared with Figure 16, it shows almost no corrosive effects, demonstrating the random nature of the corrosion behavior. Thus, it was concluded that TIG-welded titanium would not be suitable in the PWR environment because of its unpredictable corrosive nature.

The LASER welds, however, exhibited more desirable behavior. Titanium in the form of 0.050-inch diameter tubing was used to simulate a small-diameter titanium-sheathed thermocouple. Figure 19 shows such a weld. A series of overlapping beam bursts was made at the tip of the flattened tube to effect the weld. The material splatter was a typical result of the ruby LASER welds. Similar welds made with an yttrium-aluminum-garnet LASER were reported to be splatter-free[17]. Figure 20 shows a weld after 2500 hours of testing. A small amount of possible corrosion product was visible at the Zircaloy-weldment interface. Figure 21 shows a section of a LASER weld after 1000 hours of testing. No noticeable material loss was evident. This figure shows the virtual absence of a heat-affected region in the Zircaloy. The dissimilar-metals joint interface is still present with the LASER weld, but no grain growth in the Zircaloy is evident.

Also, no random examples of excessive corrosion were seen in the LASER welds as were seen in the TIG welds. This was probably due to the fact that the LASER weldments were performed very rapidly (milliseconds compared

7.8X Specimen 15-5

Fig. 18 Titanium foil TIG welded to Zircaloy and tested for 2000 hours. Compare this specimen with that in Figure 16.

7.8X Specimen 23-30

Fig. 19 Titanium tubing LASER welded to Zircaloy. This specimen was untested.

7.8X Specimen 23-34

Fig. 20 Titanium tubing LASER welded to Zircaloy. This specimen was tested for 2500 hours. A small amount of possible corrosion product is seen at the surface of the Zircaloy-weldment interface.

55X Specimen 23-22

Polarized Light

Fig. 21 Titanium tubing LASER welded to Zircaloy. This specimen was tested for 1000 hours. No material loss was evident. Note the absence of a heat-affected region at the weld.

to seconds for a TIG weld), and intermixing of the titanium and Zircaloy was limited. This was one reason that led to the recommendation to use LASER-welded titanium for this application.

2.4 Tantalum

Tantalum corrosion coupons were initially bluish-gray in color, typical of the metal. As the test progressed, the color changed gradually to a dark brown. Surface microcracks and spalling layers were seen toward the end of the test (see Figures 22 and 23). It was known that the corrosion coupons were cold worked somewhat. No attempt was made to control the temper of the metal. Figure 22 shows that the cracking was parallel to the direction of rolling of the metal.

7.8X Specimen 18-15

Fig. 22 Tantalum corrosion coupon after 2500 hours of testing. The shadows seen here were cast by a thin layer which had lifted from the surface of the base metal. The edge along which this occurred was parallel to the direction in which the material was rolled.

50X Specimen 18-15

Bright Field

Fig. 23 Cross section of tantalum corrosion coupon of Figure 22.

Studies of the tantalum-zirconium system indicated extensive solid solubility[18], suggesting good weld compatibility with Zircaloy. Specimens were fabricated by TIG welding 0.010-inch thick tantalum foils to Zircaloy tubing. A typical weldment is shown in Figure 24. A section of the weld is shown in Figure 25. A large amount of Zircaloy was displaced during the welding process due to the much higher melting temperature of the tantalum.

7.8X Specimen 16-1

Fig. 24 Tantalum foil TIG welded to Zircaloy. This specimen was untested.

50X Specimen 16-1

Polarized Light

Fig. 25 Tantalum foil TIG welded to Zircaloy. This specimen is a section of that shown in Figure 24. The loss of Zircaloy was due to complete melting, caused by the very high temperature required to melt the tantalum.

The weld areas exhibited rapid corrosion during the test. Figure 26 shows a specimen after 500 hours of testing, and Figure 27 shows one after 2500 hours. The weld areas were covered with a yellowish-brown oxide layer which readily spalled from the base metal. Large amounts of material loss resulted, rendering this attachment unsuitable in a PWR environment.

Note in Figure 27 that preferential oxidation along various crystalline axes in the Zircaloy has resulted in a dramatic exposure of the large grain structure near the weld. (This structure is usually not seen unless the specimen is etched and observed in polarized lighting.)

7.8X Specimen 16-2

Fig. 26 Tantalum foil TIG welded to Zircaloy. This specimen was tested for 500 hours. Compared with Figure 18, the weld area has become white with oxide. Spalling was evident.

7.8X Specimen 16-6

Fig. 27 Tantalum foil TIG welded to Zircaloy. This specimen was tested for 2500 hours. Large amounts of oxide were evident in the weld.

2.5 Niobium-1% Zirconium

Niobium-1% zirconium corrosion specimens were prepared from annealed bar stock. They were initially metallic gray, but changed to brown and then to a mottled grayish-black as the test progressed. Extensive pitting was observed. The extreme amount of material loss was detected also by the settlement of niobium oxide (in the form of a sludge) in the bottom of the autoclave. Figure 28 shows the appearance of the NB-1Zr surface after 2500 hours of testing. The corrosion rate of Nb-1Zr was uncommonly rapid compared to the other materials. Figure 29 shows a group of 0.032-inch diameter Nb-1Zr-sheathed thermocouples tested for just 500 hours. Complete sheath failure occurred. The sheath oxidized heavily and embrittled, resulting in splitting, spalling, and subsequent exposure of the white, compacted magnesium oxide insulation. This behavior rendered Nb-1Zr unsuitable for use in a PWR environment.

7.8X Specimen 4-14

Fig. 28 Niobium-1% zirconium corrosion specimen tested for 2500 hours.

7.8X

Fig. 29 Niobium-1% zirconium-sheathed thermocouples tested for 500 hours. Complete sheath failure resulted.

IV. CONCLUSIONS

Results of the corrosion tests indicated that both niobium-1% zirconium and tantalum were unsuitable for long-term use in a PWR environment. While pure platinum was essentially unaffected by the high-temperature water environment, the platinum-to-Zircaloy weld area showed excessive corrosion and embrittlement. Although Zircaloy was suitable from a corrosion standpoint, its availability as small-diameter thermocouple sheathing was still questionable.

Of the materials tested, titanium was best suited to the application in terms of corrosion resistance, weldability to Zircaloy, and availability. Therefore, it was recommended that titanium be used as the sheath material for thermocouples installed on fuel pins in the LOFT reactor. Titanium would provide a service lifetime of the thermocouples of at least 2500 hours.

V. REFERENCES

1. Thomas F. Demmitt, "Corrosion and Its Effects in Nuclear Power Plant Systems", BNWL-SA-3807 (May 1971).
2. R. S. Flemons, "Attachment of Thermocouples to Zircaloy Tubes by Induction Brazing", R-69-CAP-8 (May 30, 1969).
3. R. S. Flemons and A. D. Lane, "Thermocouples for Surface Temperature Measurement in Multielement Nuclear Fuel Bundles", a paper presented at the Fifth Symposium on Temperature, Washington, D. C. (June 21-24, 1971).
4. S. Kass, "Further Studies Defining the Aqueous Corrosion Performance of a Zirconium-Niobium-Copper Alloy", WAPD-TM-754 (April 1970) p. 14.
5. D. E. Thomas, "Corrosion in Water and Steam", from The Metallurgy of Zirconium, Benjamin Lustman and Frank Kerze, Jr. (eds.), New York: McGraw-Hill Book Company, Inc. (1955) p. 633.
6. A. B. Johnson, Jr., "Parameters Which Influence the In-Reactor Corrosion of Zirconium Alloys", BNWL-SA-1719 (May 2, 1968).
7. J. E. LeSurr and P. E. C. Bryant, "The Effect of Water Chemistry on the Oxidation of Zirconium Alloys Under Reactor Radiation", AECL-2797 (February 1968).
8. G. Ullrich, "Breakaway Mechanism During the Corrosion of Zirconium", WAPD-TM-122 (1968).
9. W. D. Klopp, W. E. Berry, and D. J. Maykuth, "The Hot Water Corrosion Resistance of Columbium and Columbium Alloys", from Columbium Metallurgy, D. L. Douglass and F. W. Kunz (eds.), New York: Interscience Publishers (1961) pp. 695, 701, 716.
10. M. G. Fontana and N. D. Greene, Corrosion Engineering, New York: McGraw-Hill Book Company, Inc. (1967) pp. 347-348.
11. W. B. Jepson and S. J. Gregg, "Discontinuous Oxide Films", from Corrosion, Volume I, Corrosion of Metals and Alloys, L. L. Shreir (ed.), New York: John Wiley & Sons, Inc. (1963) p. 1.169.
12. D. D. Keiser, private communication (June 11, 1970).
13. J. C. Downey, private communication (June 11, 1970).
14. K. Hauffe, Oxidation of Metals, New York: Plenum Press (1965) p. 211.
15. E. T. Hayes and W. L. O'Brien, "Zirconium Equilibrium Diagrams", from The Metallurgy of Zirconium, Benjamin Lustman and Frank Kerze Jr., (eds.), New York: McGraw-Hill Book Company, Inc. (1955) pp. 476-477.

16. J. B. Cotton, "Titanium and Zirconium", from Corrosion. Volume I. Corrosion of Metals and Alloys, L. L. Shreir (ed.), New York: John Wiley & Sons, Inc. (1963) pp. 5, 47.
17. J. C. Downey, private communication (September 9, 1971).
18. E. T. Hayes and W. L. O'Brien, "Zirconium Equilibrium Diagrams", from The Metallurgy of Zirconium, Benjamin Lustman and Frank Kerze, Jr. (eds.), New York: McGraw-Hill Book Company, Inc. (1955) p. 472.

VI. BIBLIOGRAPHY

1. Amaev, A. D. et al, "Study of the Behavior of Zirconium Alloys in Water and Steam-Water Mixtures in the MR Reactor Loops", LB G-3006 (1969).
2. Aqua, E. N. et al, "Corrosion and Hydriding of Zircaloy Under Heat Transfer Conditions", WCAP-3269-56 (August 1967).
3. Asher, R. C., "The Oxidation and Hydriding of Zirconium Alloys Under Irradiation in Steam", GCM UK B-8 (March 1964).
4. Beck, F. H. et al, "Stress Corrosion Cracking of Titanium Alloys", NASA-CR-117177 (December 1970).
5. Beranger, G. et al, "Study of Corrosion and Protection of Zirconium and Its Alloys. Germination and Growth Phenomena During the Surface Oxidation of Zirconium", WAPD-Trans-11 (1965).
6. Berry, W. E., "Corrosion by Aqueous and Gaseous Media", Reactor Materials 12:2 (Summer 1969).
7. Blanchet, J. et al, "The Effect of Radiation on the Corrosion of Zircaloy-2 in Aqueous Solutions at High Temperatures", WAPD-Trans-87 (1967).
8. Boulton, J., "Current Knowledge of Zirconium Alloys for Reactor Usage", AECL-3365 (June 1969).
9. Cerrai, E. et al, "Further Experiments on the Corrosion Rate of Zircaloy-2 in Steam-Water Mixture Under Reactor Radiations", CISE-R-290 (October 1969).
10. Chaudron, G., "Study of Corrosion and Protection of Zirconium and Its Alloys", WAPD-Trans-114 (1966).
11. Demmitt, Thomas F., "Corrosion and Its Effects in Nuclear Power Plant Systems", BNWL-SA-3807 (May 1971).
12. Douglass, D. L. and F. W. Kunz (eds.), Columbium Metallurgy, New York: Interscience Publishers (1961).
13. Flemons, R. S., "Attachment of Thermocouples to Zircaloy Tubes by Induction Brazing", R-69-CAP-8 (May 30, 1969).
14. Flemons, R. S. and A. D. Lane, "Thermocouples for Surface Temperature Measurement in Multielement Nuclear Fuel Bundles", a paper presented at the Fifth Symposium on Temperature, Washington, D.C. (June 21-24, 1971).
15. Fontana, Mars G. and Norbert D. Greene, Corrosion Engineering, New York: McGraw-Hill Book Company, Inc. (1967).
16. Gadiyar, H. S., "Current Trends on Aqueous Corrosion of Zirconium Alloys: A Review", BARC-463 (1970).

17. Galonian, G. E., "Corrosion of Structural Materials in Water-Cooled Power Plants", KAPL-P-3929 (January 19, 1971).
18. Hauffe, Karl, Oxidation of Metals, New York: Plenum Press (1965).
19. Johnson, A. B. Jr., "Parameters Which Influence the In-Reactor Corrosion of Zirconium Alloys", BNWL-SA-1719 (May 2, 1968).
20. Kass, Stanley, "Further Studies Defining the Aqueous Corrosion Performance of a Zirconium-Niobium-Copper Alloy", WAPD-TM-754 (April 1970).
21. Kofstad, Per, High-Temperature Oxidation of Metals, New York: John Wiley & Sons, Inc. (1966).
22. Kreig, A., "Dynamic Sorcening Corrosion Tests of Yankee Materials of Construction In High Temperature Borated Water", YAECL-116 (1959).
23. Kubaschewski, O. and B. E. Hopkins, Oxidation of Metals and Alloys, New York: Academic Press, Inc. (1962).
24. LeSurr, J. E. and P. E. C Bryant, "The Effect of Water Chemistry on the Oxidation of Zirconium Alloys Under Reactor Radiation", AECL-2797 (February 1968).
25. Lowe, A. L., Jr. and C. R. Johnson, "Corrosion and Hydriding of Zircaloy. Task 2 Topical Report. Effects of Hydrogen and Precipitated Hydrides on Mechanical Properties of Zircaloy-4", BAW-3765-6 (March 1968).
26. Lustman, Benjamin and Frank Kerze, Jr. (ed.), The Metallurgy of Zirconium, New York: McGraw-Hill Book Company, Inc. (1955).
27. Mottern, D. J., "Oxidation of Certain Refractory Alloys", SC-DR-70-164 (November 1970).
28. Nomura, S., "Corrosion of Reactor Materials Under Irradiation", NASA-TT-F 13093 (July 1970).
29. Nomura, Sueo and Cho Akutsu, "Oxidation Kinetics and Oxide Film Break-Away of Zirconium and Its Alloys at High Temperatures", JAERI-1161 (March 1968).
30. "Papers Presented by AECL and CGE Staff at the UK Canada Symposium on Zirconium and Its Alloys, Chalk River", GMI-15 (September 1962).
31. Roesler, Ulrich and Hartmut Rubel, "Zirconium as Material for the Reactor Core", WAPD-Trans-119 (1968).
32. Rubright, M. M. et al, "Corrosion and Hydriding of Zircaloy", BAW-3765-7 (1969).
33. Shreir, L. L. (ed.), Corrosion. Volume I, Corrosion of Metals and Alloys, New York: John Wiley & Sons, Inc. (1963).

34. Shreir, L. L., (ed.), Corrosion. Volume II, Corrosion Control, New York: John Wiley & Sons, Inc. (1963).
35. Symposium on High-Purity Water Corrosion, ASTM Special Technical Publication No. 179, Philadelphia: American Society for Testing and Materials (1956).
36. Ullrich, Georg, "Breakaway Mechanism During the Corrosion of Zirconium", WAPD-TM-122 (1968).
37. Whyte, D. D., "A Long Term Corrosion Test of Reactor Structural Materials in a Chemical Shim Solution", WCAP-3737 (March 1964).