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**ZIRCONIUM HYDRIDE FORMATION IN
HANFORD PRODUCTION REACTOR
PROCESS TUBES**

W. K. WINEGARDNER
AND
B. GRIGGS

DECEMBER 1967

**AEC RESEARCH &
DEVELOPMENT REPORT**

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ZIRCONIUM HYDRIDE FORMATION IN HANFORD
PRODUCTION REACTOR PROCESS TUBES

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ZIRCONIUM HYDRIDE FORMATION IN HANFORD
PRODUCTION REACTOR PROCESS TUBES

ABSTRACT

Examination of Zircaloy-2 process tubes from Hanford Production Reactors has revealed extensive zirconium hydride formation. In general, attack is limited to the downstream portions of tubes where aluminum spacers are located. Most of the hydride platelets are contained in a case or layer on the inner surface of the tube. It is not unusual to find cases 0.004 to 0.005 in. thick. Analyses of the 0.037 in. wall tubes with such cases intact often reveal hydrogen concentrations greater than 1000 ppm. Investigation indicates that the hydriding is the result of galvanic contact between aluminum and Zircaloy-2. The galvanic couple (contact between dissimilar metals in the presence of reactor cooling water which serves as the electrolyte) results in the cathodic charging of hydrogen into the Zircaloy.

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ZIRCONIUM HYDRIDE FORMATION IN HANFORD
PRODUCTION REACTOR PROCESS TUBES

W. K. Winegardner and B. Griggs

INTRODUCTION

Predictions of limited life resulted in the replacement of aluminum process tubes of two Hanford Production Reactors with those fabricated from Zircaloy-2. It was expected that the substitute tubes would last for the life of the reactor since extrapolation of high temperature aqueous corrosion data for Zircaloy-2 indicated negligible corrosion would occur. Examination after about two years of service, however, revealed extensive zirconium hydride formation. Because embrittlement effects arising from the formation of this compound could drastically affect the expectation that the tube service life would be equal to the life of the reactor, an intensive investigation of the phenomenon was prompted. This report summarizes information arising from the investigation of the extent and nature of the hydriding.

The report also discusses the investigation of several of the processes which, at one time or another, were felt to be involved in the attack. The hydriding phenomenon was finally linked to the fact that Zircaloy-2 is the cathode of a galvanic couple. It should be noted that at the time the tubes were installed, little experience had been obtained concerning the exposure of Zircaloy-2 to an environment where galvanic effects, especially cathodic reactions, played an important role.

Results of tests related to both proposed mechanisms and possible remedial measures are presented in the report. Also included are test results associated with the investigation of the possibility of tube embrittlement resulting from hydrogen migration from existing hydride layers into the underlying metal even after attack is stopped. No discussion of the effect of hydride formation on specific mechanical properties is included.

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SUMMARY

Investigation of the extent of attack indicates that all Zircaloy-2 process tubes equipped with aluminum spacers are hydrided to some degree. Thirty-four tubes have been examined and all were hydrided. In general, attack is limited to the downstream portions of tubes where the spacers are located. Most of the hydride platelets are contained in a case or layer on the inner surface of the tube. It is not unusual to find hydride cases 0.004 to 0.005 in. thick. Analyses of the 0.037 in. wall tubes with such cases intact, often reveal total hydrogen concentrations greater than 1000 ppm. Hydrogen concentrations of 50 to 80 ppm are routinely found in the tube material underlying the hydride case. Even the latter concentrations are five to ten times higher than that found in tube material with no exposure.

Investigation of possible mechanisms indicates that the hydriding of the process tubes is a result of galvanic contact between Zircaloy-2 and aluminum. Low temperature reactor cooling (process) water serves as the electrolyte. Tests have shown repeatedly that the galvanic couple formed by aluminum and zirconium alloys in low temperature process water can result in hydrogen pickup and hydride case formation in the zirconium alloy, the cathode of the couple. This cathodic charging of hydrogen into Zircaloy-2 by a galvanic couple has been demonstrated both in-reactor and out-of-reactor.

In tests to evaluate potential remedial techniques, replacement of aluminum with materials cathodic to Zircaloy-2 stopped the formation of hydride. Oxide films, formed by either anodizing aluminum or autoclaving zirconium, have been investigated as methods of insulating one material from the other. The use of anodized aluminum spacers prevented hydride formation in a "new" process tube. In coupon tests, metallography revealed that autoclaving of Zircaloy-2 prevented uniform case hydriding, but local attack did occur at imperfections or breaks in the oxide film.

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Tests have also been conducted to investigate the effect of continued exposure on hydride distributions after attack has been stopped. These tests indicate that there is no migration of hydrogen from the dense case on the inner surface of the tube into the underlying material if further introduction of hydrogen to the system is eliminated.

DISCUSSION

Cooling water leaks prompted the temporary shutdown of one of the Hanford Production Reactors during March, 1965.⁽¹⁾ Leak testing during this shutdown revealed the necessity of removing two of the Zircaloy-2 process tubes. Indications of tube embrittlement observed during tube removal suggested the possibility of zirconium hydride formation. Subsequent metallographic examination revealed a thick case of hydride platelets on the inner surface of both tubes. Before discussing details of the attacks, certain features of the production reactors will be briefly described to provide background information.

REACTOR DESCRIPTION

Hanford Production Reactors are graphite moderated and light water cooled. The reactor core consists of an almost cubical stack of graphite. The process tubes are located in horizontal channels that penetrate the graphite stack front to rear. The tubes contain aluminum clad, metallic uranium fuel elements, and they direct single-pass cooling (process) water past the fuel elements to remove the heat produced by fission. Process tubes are longer than the core to allow penetration of the shielding that surrounds the core. Only the portions of the tubes lying within the core contain fuel elements. The length of tube extending through the rear shielding contains several eight-inch long aluminum spacers for centering the fuel charge. Cooling water enters the tubes at the front, and the spacers prevent the high pressure water from washing the fuel elements downstream, i. e., away from the reactor core. The relative location of the various downstream reactor components is shown in Figure 1.

FIGURE 1. Location of Reactor Components

[REDACTED]

Fuel elements are clad with aluminum alloy 8001 and are autoclaved prior to reactor use to assure cladding integrity. Spacers are fabricated from aluminum alloy 6063 but are not autoclaved. In addition to the difference in alloy, there is an autoclave (surface oxide) film present on the fuel elements but not on the spacers. One type of spacer geometry is shown in Figure 2. (The spacer shown in this figure is not standard in that it has been slotted to permit the in-reactor exposure of coupons.)

Initially, all process tubes were aluminum. Limited service life for aluminum tubes, however, led to their replacement in two reactors, KE and KW Reactors. The substitute tubes were fabricated from the zirconium alloy Zircaloy-2 (about 1.5% tin, 0.12% iron, 0.10% chromium and 0.05% nickel). Prior to this full scale replacement 69 Zircaloy tubes had been installed in C Reactor and two prototype tubes in KW Reactor. The final tube reduction process for the tubes used in the full scale replacement left the 1.8 in. OD by 0.037 in. wall tubes with about 35% cold work. The Zircaloy tubes entered reactor service in the surface sanded condition, i. e., without any protective (autoclave) zirconium oxide film. ⁽¹⁾

Reactor cooling water is Columbia River water that has been subjected to alum flocculation, settling, and filtration. In addition, pH is adjusted slightly acidic with sulfuric acid (pH currently 6.6), and the water contains about 1 ppm sodium dichromate. Specific resistivity at 20 °C is about 6500 Ω -cm.

EXTENT OF HYDRIDING ^(2, 3, 4, 5, 6)

Metallographic examination of the two Zircaloy-2 reactor process tubes removed during 1965 because of water leaks (tubes 3065-KW and 3075-KW) revealed a thick case of hydride platelets on the inner surface of the tubes. Examination also revealed that extensive attack was limited to the downstream portion of the tubes where the aluminum spacers are located. Although failure of the two tubes was never related solely to

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[REDACTED]

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FIGURE 2. Spacer (Coupon Holder) Geometry

[REDACTED]

the hydride, attack was extensive enough to suggest the possibility of reduced tube life and a program was immediately begun to further define its extent. To date, samples from 34 Zircaloy-2 reactor tubes that were charged with standard aluminum spacers have been examined. Without exception, hydride was found similar in extent to that described above for the first two tubes. In addition, it was observed that although most of the hydrogen is contained in the case, the concentration of metal underlying the case is significantly higher than that of tube material with no in-reactor exposure.

All but two of the tubes examined were from KE and KW Reactors. Both metallography and vacuum extraction analyses have been used to investigate the extent of attack. The metallographic procedure includes a chemical etch of a cross-section of the tube wall with a solution consisting of 45 parts by volume concentrated (70%) HNO_3 , 45 parts water, and 8 to 10 parts concentrated (48%) HF .⁽⁷⁾ The hydrogen concentration of samples is determined by a low pressure, hot extraction technique in which the samples are inductively heated and the partial pressure of the evolved hydrogen gas is measured.

The results of the vacuum extraction analyses for many of the tubes examined to date are presented in Appendix A. In the remainder of this section of the report, selected analyses and photomicrographs will be used to illustrate the extent and nature of the attack.

Radial Distribution

Figure 3, a photomicrograph of a typical severely hydrided area, shows the inner surface and a portion of the underlying tube wall of process tube 3966-KW. The particular area shown was originally located about 9 in. from the downstream end of the tube. Tube 3966-KW had been in service in KW Reactor for 25 months. The dense case of hydride platelets on the inner surface of the tube is one of the most obvious features revealed by metallographic examination. Vacuum analysis of

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0.004 in.

Neg 466-1903

250X

Inner Surface of Process Tube 3966-KW
Exposure - 25 mo

FIGURE 3. Hydride Case Resulting From
In-Reactor Exposure

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material immediately adjacent to that shown in Figure 3, revealed hydrogen concentrations of 1355 ppm with the case intact and 75 ppm after removing the case. About 95% of the hydrogen is contained in the case. If it is assumed that hydrogen is uniformly distributed in a 0.004 in. thick case and the density of the case is not significantly different than that of the Zircaloy, a value of about 1.5 is calculated for the atomic ratio, H/Zr.

The thickest case observed to date, 0.012 in., was associated with Tube 1578-KW. This tube was exposed in KW Reactor for 44 mo. The hydrogen concentration determined for a tube sample with the 0.012 in. case intact was 2480 ppm. The case was found on a tube sample which was originally located about 7 in. from the downstream end of the tube. In a few instances, cases were observed where the population of hydride platelets was not as dense as that shown in Figure 3. A close examination will reveal that the platelets in the portion of the case immediately adjacent to underlying material are not as closely spaced as those in the remainder of the case. This transition in platelet density was observed often, and in many instances was more pronounced than indicated in Figure 3.

In the remainder of the report, the underlying material or that portion of the tube wall other than that associated with the case of hydride platelets, will be referred to as base metal. As previously indicated, the hydrogen concentration in material underlying the case (the base metal concentration) is significantly higher than that found in tubes with no in-reactor exposure. The base metal concentration shown in Figure 3 is about 75 ppm; analyses of new K Reactor tubes has suggested an initial concentration of about 10 ppm.

The base metal shown in Figure 3 is representative of all of the tube wall underlying this particular case. Except for the case, no obvious radial concentration gradients have been observed in the tube wall.

[REDACTED]

It is of interest to note that the relatively high base metal concentration is not immediately apparent from metallography; the extent and/or fine structure of platelets in the base metal shown in Figure 3 does not suggest a concentration of 75 ppm. As shown in Figure 4, heating a base metal sample containing about 65 ppm hydrogen, resulted in a redistribution which makes the extent of base metal hydriding more obvious by metallographic techniques.

Longitudinal Distribution

In general, hydriding is limited to the downstream length of tube where standard aluminum spacers are located. In many instances, case thickness and hydrogen concentration decreased as distance from the downstream end of the tube increased. Figure 5 is a plot of hydrogen concentration versus tube length for tube 3181-KE, while Figure 6 shows photomicrographs of the inner surface of this same tube at various distances from the downstream end. Tube 3181-KE had been exposed in KE Reactor for about 24 mo. As shown in Figure 5, analyses of the total hydrogen content (analyses with the case intact) were from three different circumferential locations. The concentration decreased with distance for all three locations. The decrease in concentration stopped, however, at a position corresponding to a distance 89 in. from the downstream end of the tube. At this distance, the hydrogen concentration had dropped to a value corresponding to the concentration that would be estimated for the tube before it was placed in service, indicating that no hydriding had occurred upstream of this point.

A similar longitudinal position, beyond which hydriding has not occurred on the upstream side, has been observed in all tubes examined. Preliminary examinations suggested that there was no hydriding beyond (upstream of) the point where the spacer charge stopped and many attempts were made to relate this to a mechanism for the attack. Continued

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Base Metal Sample
from Process Tube
3966-KW - Expo-
sure of 25 mo
Hydrogen Concen-
tration ~ 65 ppm.

Neg 467-159A

250X

Before Heating

Sample Heated to
500 °C, Held
3 hr at Tempera-
ture and Slow
Cooled.

Neg 467-158A

250X

After Heating

FIGURE 4. Effect of Heating Base Metal Sample

FIGURE 5. Longitudinal Distribution of Hydrogen, Process Tube 3181-KE

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FIGURE 6. Photomicrographs of the Inner Tube Surface at Various Distances From the Downstream End - Process Tube 3181-KE

[REDACTED]

examination has revealed that hydriding has occasionally occurred upstream of the end of the spacer charge. For example, hydride has been found 130 in. from the end of process tube 1972-KE or 26 in. within the fueled portion of the tube. ⁽⁸⁾

There is no intent to imply that the decrease in hydrogen concentration with distance from the downstream end of the tube can always be described with terms such as gradual, linear, or uniform. In several instances, analyses suggested a decrease with distance up to about 60 in. from the downstream end of the tube. Analyses beyond 60 in. then revealed increasing concentrations for the next 10 to 30 in., followed by a second gradient of decreasing concentration with distance until the longitudinal position where hydriding stops was reached. In a few instances, analyses indicated that attack along the downstream length of the tube was relatively uniform. Total hydrogen concentrations of 239, 202, 210 and 249 ppm were found 1, 3, 5, and 7 ft from the downstream end during examination of process tube 2557-KW (exposed 47 mo). Base metal concentration found at the same four locations were 100, 93, 84, and 133 ppm respectively. As in the case of tubes with a pronounced longitudinal gradient, an abrupt transition in the extent of attack was found. Total hydrogen content dropped by a factor of about 10, and no concentration greater than 25 ppm was observed beyond 8 ft from the downstream end of the tube.

Base metal hydrogen concentration gradients generally parallel those for total hydrogen in a given tube. In general, the type of longitudinal distribution could be determined by either analyses with or without the case intact. If total hydrogen concentration decreased as distance from the downstream end increased, then the base metal concentration similarly decreased; if total concentration was about the same along the downstream portion, then base metal concentration was about the same. The longitudinal gradient found in the base metal of tube 3181-KE is also shown in Figure 5. As in the case of total concentration, base metal hydrogen content decreased as distance from the downstream end of the tube increased.

[REDACTED]

[REDACTED]

Circumferential and Radial Distribution

The total hydrogen concentration of tube 3181-KE was determined at three different circumferential locations. Examination of Figure 5 will reveal that at a given longitudinal position, analyses at different circumferential locations often gave obviously different results for total concentration. The preceding type of distribution is illustrated in Table I which presents additional data from tube 3966-KW (also, see Figure 3). In Table I, in addition to total concentration, base metal concentration is given for two circumferential positions. Unlike longitudinal gradients, base metal concentration does not obviously conform to the circumferential gradient established by total concentration. The base metal analyses presented in Table I also illustrate the lack of a radial gradient in the base metal that was discussed earlier. As shown in the table, only slight differences in hydrogen concentration are found in punchings upon removing additional material from a particular sample.

In summary, at a given distance from the downstream end of the tube, base metal concentration appears to be relatively uniform both radially and circumferentially. The base metal concentrations above in Figure 5 are, in fact, averages of analyses from two circumferential locations about 120° apart. An average value is reported because of the uniformity in base metal concentration. Recent examinations suggest the possibility of a circumferential base metal hydrogen concentration gradient that is related to variations in tube wall thickness. This particular gradient will be discussed in the following section.

Other Observations

Initial efforts were directed toward determining how many tubes were hydrided and estimating the severity of attack. Because of the large number of tubes involved and the priority for gross tube characterization, it was difficult, at first, to undertake the analysis of a local region of an individual tube. Extensive examination may yet reveal gradients--especially local or refined gradients--other than those

TABLE I. Hydrogen Distribution-Process Tube 3966-KW⁽⁶⁾

Sample Number	Distance From Downstream End of Tube (in.)	Approx. Thickness of Hydride Case (in.)	Mils Removed From Sample (0 Indicates Case Intact)	Hydrogen ^(a) Concentration (ppm)	
				Loc. A	Loc. B
1	8 1/2 to 9 1/2	0.004	0	993	1355
	8 1/2 to 9 1/2	0.004	6	71	-
	8 1/2 to 9 1/2	0.004	9	68	75
	8 1/2 to 9 1/2	0.004	16	64	69
2	34 1/2 to 35 1/2	0.001	0	372	409
	34 1/2 to 35 1/2	0.001	5	50	50
	34 1/2 to 35 1/2	0.001	6	-	49
	34 1/2 to 35 1/2	0.001	7	46	47
	34 1/2 to 35 1/2	0.001	8	49	-
3	59 to 60	<0.001	0	280	326
	59 to 60	<0.001	9	45	-
	59 to 60	<0.001	10	-	42
	59 to 60	<0.001	11	45	-
	59 to 60	<0.001	19	-	45
	59 to 60	<0.001	20	47	-
	59 to 60	<0.001	24	-	45

(a) Location A about 120° from Location B.

previously described. Evidence of this has already arisen from more detailed analyses of base metal for radial and/or circumferential concentration gradients. As indicated in the previous section, recent examinations suggest that a circumferential base metal gradient exists where there is an appreciable variation in tube wall thickness.

Figure 7 shows the thickness and base metal hydrogen concentration of punchings taken from ring shaped sections of two process tubes. The punchings were taken from eight, equidistant circumferential positions and all punchings from a particular tube were located at the same longitudinal position. As shown in Figure 7, the higher base metal hydrogen concentrations are usually associated with the thinnest portion of the tube wall.

FIGURE 7. Base Metal Hydrogen Concentration as a Function of Wall Thickness.

Attempts have been made to relate the extent of attack with the length of time a particular tube has been installed in-reactor. Because longitudinal variation is often observed, the initial reaction was to compare analyses from various tubes at the same distance from the downstream end of the tube. A review of the data revealed this could best be done at a distance of about 12 in. and the results of this review are summarized in Table II. As shown in this table, there appears to be no obvious relationship between total hydrogen content and time. All of the base metal concentrations greater than 90 ppm, however, are associated with the tubes that had the longest service, 3 1/2 to 4 yr. Statistical analysis of data revealed an increase in base metal concentration with time of 2.2 ppm/mo.⁽⁹⁾ The preceding value was obtained from the linear data fit shown in Figure 8. The hydrogen concentrations shown in Figure 8 are the maximum base metal concentrations found in the various tubes and are also listed in Table II. The concentrations are not associated with one particular longitudinal position, but as might be expected, were usually found near the downstream end. As indicated in Reference 9, at this time there is insufficient evidence to use any function more complex than the linear one used to fit the data of Figure 8.

Before ending the section concerning the extent of attack, it should be noted that in Figure 5 and 6 information associated with extreme downstream positions of tube 3181-KE is missing. In addition, in Figure 8 the maximum base metal concentration is the maximum found in the tube except for the first 4 in. of the tube closest to the downstream end. Information associated with the extreme downstream portion was purposely deleted because of metallurgical changes arising from heat treatment when a flange is formed on the end of the tube. Such changes can affect both absorption and distribution of hydrogen, making any comparison between the local region near the end of the tube and the remaining cold worked length, inappropriate. As stated in Reference 5, "In this heat treated zone the hydride has a lacy characteristic following the boundaries of the large alpha grains. Beyond the heat treated zone, the hydride becomes compact (case hydride) with a well defined interface."

TABLE II. Hydrogen Concentrations for Process Tubes
With From 4 to 48 Mo Exposure

Tube Number	Exposure (Months)	Hydrogen Concentration (ppm) 11 to 13 in. From Downstream End		Maximum Base Metal Concentration (ppm)	Reference
		Total	Base Metal		
4372-KE3*	4	132	-	-	5
3075-KW2	4	602	16	16	3, 9
3074-KW2	7	-	-	22	9
0868-KE	12	-	-	13	9
4372-KE	14	-	-	44	9
3075-KW	19	-	-	53	9
2169-KE	22	-	-	34	9
3181-KE	24	1053, 511	76	91	6, 9
3667-KW	24	-	-	54	9
3966-KW	25	1158, 1230	58	76	6, 9
3074-KW	25	-	-	36	9
4453-KW	26	-	-	62	9
2048-KW	27	-	-	41	9
1554-KW	36	-	-	80	9
1357-KW	40	-	-	93	9
1773-KE	42	437	84	99	9
1766-KE	42	516	92	97	9
3172-KW	43	1040	98	106	9
3160-KW	43	827, 754	95	95	9
3065-KW	44	1210	113	116	3, 9
1960-KE	44	-	83	94	9
1972-KE	44	-	70	90	9
1571-KW	44	1360	110	115	9
1578-KW	44	1694, 1769	102	112	9
2571-KE	44	239	59	78	9
2577-KE	44	308	68	74	9
2557-KW	48	239	100	133	3, 9

* The last 3 in 4372-KE3 indicates that this is the third tube to be installed in a particular tube position, the same type of numbering system is used throughout the report.

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FIGURE 8. Base Metal Hydrogen Concentration as a Function of Exposure

[REDACTED]

In summary, investigation of the extent of the hydride has resulted in the following conclusions:

- All Zircaloy-2 tubes equipped with standard aluminum spacers are hydrided to some extent; most of the hydriding has occurred in the portion of the tubes where spacers are located.
- Most of the hydride is contained in a case on the inner surface of the tube, but the hydrogen concentration of underlying material (base metal) is obviously higher than that found in material with no exposure.
- Total and base metal concentrations often decrease as distance from the downstream end of the tube increases; wide circumferential variations in total concentration (case thickness) have also been observed.

HYDRIDING MECHANISM

This section of the report will discuss some of the processes which were at one time or another felt to be involved in the attack. Factors associated with the longitudinal distribution (the fact that extensive attack is limited to the downstream portion of tubes) will be discussed first only because of the early emphasis in attempting to relate this distribution to a mechanism. Before proceeding, it should be noted that experimental evidence collected to date indicates that the hydriding is the result of the galvanic couple formed by aluminum and Zircaloy with reactor cooling water serving as the electrolyte. The galvanic couple then results in conditions conducive to the cathodic charging of hydrogen into Zircaloy. Review of factors associated with the longitudinal distribution did little to define the preceding mechanism, but did suggest why little or no attack is found in the section of the tube which contains fuel elements.

Factors Associated with Longitudinal Distribution

It was reported earlier that preliminary tube examination suggested that the mechanism was operative only in the portion of tubes where spacers are located. There was an obvious inclination to relate

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chemical and physical factors, which somehow might be associated with the mechanism, to such a striking feature--in the portion of the tube where fuel elements are located it almost appeared as if the tubes were insulated from attack. Factors that could immediately be related to this pronounced transition in the extent of attack included changes in reactor radiations, mass, and materials associated with the end of fuel charge and the start of spacers.

Reactor Radiations

Neutron and gamma fluxes along the fueled length of the tube are substantially higher than those associated with the downstream length occupied by spacers. If ionizing radiations were an accelerating factor, then the initial reaction would be to expect longitudinal distributions other than those actually observed. As will be discussed later, subsequent out-of-reactor testing without ionizing radiation proved that radiation was not the necessary catalyst for hydriding to occur.

It was suggested that rather than being an accelerating factor, neutron and gamma radiation might somehow induce chemical effects that would limit hydrogen pick up. If this were the case, flux distributions could be qualitatively related to the longitudinal hydrogen distribution that was found. Corrosion was proposed as a chemical process which might be affected by radiation, and in addition, influence, even inhibit, the extent of hydriding, depending on the source of hydrogen and the hydriding mechanism involved. As stated earlier in the report, tubes were installed without any preformed protective oxide film. In-reactor exposure had not resulted in appreciable corrosion because of the relatively low coolant temperature. It was thought, however, that radiation-accelerated corrosion could result in sufficient additional film thickness in the portions of tubes containing fuel elements to at least partially protect this particular

region.^(10, 11) A thin layer of oxide could reduce current flow if attack were electrochemical, or the film might act as barrier, preventing entry of active species into the metal lattice. Experiments confirming the effectiveness of oxide film in preventing hydrogen pickup had been conducted even before the occurrence of the hydriding of production reactor tubes.⁽¹²⁾

Subsequent investigation of two process tubes showed that the length of tube associated with the fuel elements was oxidized to a greater extent than the remainder of the tube.⁽⁴⁾ Measurements confirmed that oxide films were extremely thin, but showed that weight gains associated with in-flux portions of both tubes were twice those for the out-of-flux portions. Weight gains for the in-flux portions of the two tubes, 2557-KW and 2169-KE, were 0.40 and 0.25 mg/dm² compared with 0.20 and 0.13 mg/dm², respectively, for the out-of-flux portions. Tubes 2557-KW and 2169-KE were in service for 47 and 22 mo, respectively.

Mass

Differences in mass and other physical features at the spacer-fuel element boundary could often be associated with a pronounced transition in the extent of attack. It was proposed that oscillatory motion between surfaces in contact, induced by flow variations on the relatively light spacers, could result in damage to already thin but protective oxide films. Attempts to establish the fact that attack was primarily the result of mechanical damage to films were unsuccessful.

Materials

It has already been noted that spacers are fabricated from one type of aluminum alloy, type 6063, while fuel elements are clad with another, type 8001. As will be shown in a following section, differences in aluminum alloy composition were more important than originally expected. Briefly, the amount of hydrogen which can be cathodically introduced is significantly affected by the aluminum alloy to which Zircaloy-2 is coupled.

Pretreatment

The fact that fuel elements were autoclaved and spacers were not, was one of the first features discussed in relationship to the hydriding. If attack were electrochemical, an aluminum oxide film from the autoclaving process, like a zirconium oxide film, could assist in reducing corrosion rates and the resulting corrosion (hydriding) currents.

Cathodic Charging of Hydrogen

The phrase--if attack were electrochemical--was purposely used several times in the previous section since electrochemical processes have been linked not only with corrosion (oxidation), but also with hydrogen pickup. This link is established by the fact that hydrogen ion reduction occurs at the cathode of electrochemical cells with aqueous electrolytes. Increased concentrations of hydrogen atoms, arising from the reduction and then adsorbed on the cathode surface, can initiate the entry of hydrogen into the lattice of certain metallic electrodes.⁽¹³⁾ This method of introducing hydrogen, sometimes termed cathodic charging, had been demonstrated as a method of forming zirconium hydride with an applied potential.⁽¹⁴⁾ Contact between dissimilar metals in the presence of an electrolyte could also result in the driving potential for cathodic charging, and the fact that aluminum alloys are used in contact with the Zircaloy-2 tubes became one of the more obvious considerations in the review of possible causes. This led to a series of tests which showed that aluminum, coupled with Zircaloy-2 in low temperature process water, resulted in a galvanic potential (and, therefore, a current density) of sufficient magnitude to initiate cathodic charging of hydrogen. The series included both in-reactor and out-of-reactor tests, i. e., tests with and without ionizing radiation.

Out-of-Reactor Tests with Applied Potentials

Applied dc potentials rather than the galvanic potential arising from the coupling of dissimilar metals were used in the initial out-of-reactor investigation of cathodic charging. An early significant test,

reported in References 15, 16, and 17, studied hydrogen pickup with applied potentials of 0.5, 1.5, 3.0 and 4.5 V. Stainless steel anodes were used while cathodes were Zircaloy-2 coupons with an initial hydrogen concentration of about 20 ppm. The electrolyte was reactor process water at 90 °C. Approximate current densities associated with the four potentials were 0.2, 6, 300, and 900 $\mu\text{A}/\text{cm}^2$, respectively. Results of this initial work are summarized in Table III, which lists the hydrogen content found in the various Zircaloy-2 cathodes as a function of time. Metallography revealed that, as in the case of the reactor tubes, cathodic charging with an applied potential resulted in a case or layer which contained most of the hydrogen. The hydride case formed on one of the Zircaloy-2 coupons associated with the cell, with an applied potential of 4.5 V, is shown in Figure 9. The case shown in Figure 9 was formed in only 377 hr and is similar in appearance to the case shown in Figure 3, resulting from in-reactor exposure.

TABLE III. Hydrogen Pickup in Zircaloy Cathodes As a Function of Applied Potential and Time⁽¹⁵⁻¹⁷⁾

Time (hr)	Hydrogen Concentration (ppm)* dc Potentials (V)			
	0.5	1.5	3.0	4.5
138	27	31	400	860
377	27	34	1230	1700
815	35	43	1610	2050
1983	52	88	3580	4120

* Initial Hydrogen Concentration, 20 ppm.

As shown in Table III, potentials as low as 0.5 V were capable of introducing hydrogen into the cathodes. Of major significance was the fact that potentials of this order of magnitude might be expected from galvanic potentials arising from the contact of dissimilar materials. It is of interest to note that the cathode associated the lowest potential (and therefore lowest current density) is significantly more efficient in absorbing

Zircaloy-2 Cathode After 377 hr

FIGURE 9. Hydride Case Resulting from Applied Potential

hydrogen that is formed by current flow. This efficiency can be compared by calculating the ratio of increase in hydrogen content actually found, to that which would occur if all hydrogen formed by current flow were absorbed. A ratio of about one is calculated for the tests that used an applied potential of 0.5 V. This compares to a calculated value of only 0.03 for tests using a potential of 4.5 V and exposures of 815 and 1983 hr. If it is assumed that hydriding proceeds by hydrogen ion reduction on the cathode surface, then in the case of 0.5 V potential essentially all surface atoms enter the metal lattice. In the case of the 4.5 V potential, most of the surface atoms combine and are released to the environment as hydrogen gas.

A second series of out-of-reactor tests using applied dc potentials was recently initiated using an apparatus different from the one shown in Figure 9. Briefly, electrolytic cells of the second test facility consist of cylindrical platinum anodes (Pt foil supported by a lucite rod) surrounded by cathodes fabricated from sections of reactor process tube. The electrolyte is reactor process water at about 90 °C. Initial tests resulted in an increase in the hydrogen concentration of the tubular cathodes. After 328 hr, current densities of 12, 0.8 and 0.08 mA/cm² resulted in hydrogen concentrations of 958, 664, and 313 ppm, respectively. Initial hydrogen concentration was about 12 ppm. The preceding results again suggest hydrogen pickup by a mechanism that is more efficient at lower current densities (potentials). Perhaps of greater interest is the fact that analyses of the base metal content of the tube sections after the 328 hr exposure suggested that the test resulted in no hydrogen pickup. The latter indication is currently attributed to a low rate of increase in base metal concentration.

Out-of-Reactor Tests with Galvanic Couples

Applied voltages with a value not appreciably different from those that could be expected from galvanic couples were shown to be capable of initiating hydriding. As yet, however, no data was available to positively link the galvanic potential arising from a neptunium-aluminum alloy couple to the attack. Bench-top experiments have provided such data. In these

tests, Zircaloy-2 samples were coupled to both 6063 and 8001 aluminum alloys in reactor process water at 90 °C. Initial hydrogen concentration of the Zircaloy samples was about 20 ppm. After 1000 hr of exposure, the concentration of the Zircaloy sample coupled to the 6063 Al had increased to 65 to 75 ppm. The concentration of Zircaloy coupled to the 8001 Al also increased but only to 33 to 40 ppm.⁽¹⁵⁾ Galvanic potentials, ranging from 0.6 to 1.1 V have been established by coupling aluminum and zirconium alloys in process water at about 90 °C.

In-Reactor Tests

It remained to demonstrate that in-reactor hydriding was also the result of a galvanic couple and in-reactor tests were initiated to accomplish this as well as investigate remedial techniques. The assumption of cathodic charging arising from the contact of dissimilar materials suggested the investigation of obvious remedial measures, e. g. , the use of alternate spacer materials cathodic to zirconium or the prevention of galvanic contact by insulating one material from the other. The use of alternate materials was investigated in two ways: (1) Zircaloy-2 coupons have been exposed in-reactor in holders both cathodic and anodic to the coupons and (2) spacers fabricated from materials other than aluminum have been charged in process tubes. Oxide films, formed by either anodizing aluminum or autoclaving zirconium, have been used to investigate the effect of insulating one material from the other.

Coupon Tests. As a result of the early recognition that Zircaloy-aluminum couples might result in the cathodic charging of hydrogen into the Zircaloy, coupon holders of Type 304 SS were fabricated and aluminum spacers modified to accept coupons. These holders allowed the in-reactor exposure of Zircaloy-2 coupons in contact with materials both cathodic (SS holders) and anodic (aluminum) to the coupon, i. e. , under conditions which should be not conducive and which should be conducive to attack, respectively.

Figure 2 shows the type of coupon used along with a typical aluminum coupon holder (modified spacer). Stainless steel holders were similar in appearance except that a slotted, removable sleeve was used to retain the coupons instead of machined slots in the body of the holder. As shown in Figure 2, holders were designed to allow the exposure of curved coupons machined directly from actual process tubes. In addition to permitting the exposure of as-received process tube material, coupon holders allowed the exposure of Zircaloy-2 coupons with a variety of surface treatments, as well as coupons fabricated from other alloys of zirconium. The various types of coupons that have been exposed are listed in Table IV along with the total hydrogen concentration found after exposure. The table is a summary of information previously presented in References 4, 6, 17 and 18. Two values are given for many of the coupon-holder combinations since an individual holder often contained two coupons of the same type. Individual values are often averages of more than one analysis of a single coupon.

Review of Table IV will show that exposure of coupons, first machined from Zircaloy-2 process tubes and then without any additional surface treatment installed in aluminum holders, almost always resulted in obvious increases in hydrogen concentration. Results of analyses of coupons that were exposed in stainless steel holders were in obvious contrast to those obtained from coupons that were exposed in aluminum holders. Perhaps the most striking feature associated with the data of Table IV is that exposure in the stainless steel holders (i. e., exposure under conditions that do not promote cathodic charging) resulted in no obvious significant increase in hydrogen concentration.

As indicated earlier, many of the coupons were given surface treatments, sometimes in an attempt to investigate the effect of a possible remedial measure. None of the pretreatments were completely effective in eliminating hydriding when the coupon was exposed in an aluminum holder. Metallography revealed that autoclaving prevented uniform case hydriding, but hydriding did occur where there were imperfections in the

TABLE IV. Total Hydrogen Concentration (ppm) Found in Coupons After In-Reactor Exposure

Tube Number	✓	Exposed in 6063 Aluminum Holders										Exposed in 304 SS Holders				
		2384-KE	2364-KE	2364-KE	2384-KE	2384-KE	3877-KW	4166-KW	4166-KW	3878-KW	2952-KE	2952-KE	2364-KE	4370-KW	3877-KW	3878-KW
Exposure, Operating Time	0	30	37	60	67	97	106	168	168	247	~30	~60	37	106	106	247
Type of Coupon																
Process Tubing, as received, vapor blasted one side	6	65 55	150 46	36 148	65 63	122 -	274 154	45 101	41 11	243 202	148 -	7 6	5 8	5 10	- 5	- 6
Process Tubing as received	4	24 15	12 5	26 7	19 24	21 6	- -	24 7	25 10	- -	10 13	5 6	7 6	8 4	- -	- -
Process Tubing as received and autoclaved 25°C for 61 hr	25	19 20	20 21	47 23	23 17	19 18	- -	19 19	28 29	- -	35 34	40 28	19 30	24 29	- -	- -
Process Tubing as received and anodized 100 V KOH	4	41 5	5 41	5 6	39 39	92 67	- -	7 6	8 16	- -	51 38	34 32	7 4	7 4	- -	- -
Process Tubing as received and air oxidized 50°C for 10 min	5	49 55	46 92	6 10	54 55	90 90	- -	13 74	110 6	- -	7 52	139 141	7 6	5 9	- -	- -
Zr-2 Sheet, as received, vapor blasted one side	22	635 650	- -	24 676	- -	634 633	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Zr-4 Sheet, as received, vapor blasted one side	10	259 173	333 836	48 305	183 -	313 -	- -	156 166	270 257	- -	19 148	332 255	14 13	10 14	- -	- -
Zr-2, 1/2 Nb, Machined one side, vapor blasted one side	8	- -	13 65	- -	80 60	- -	- -	42 57	44 54	- -	45 23	57 42	7 7	7 9	- -	- -

oxide film. The other alloys of zirconium tested, Zr-4 and Zr-2 with 0.5 wt% Nb added, appeared to be as susceptible or even more susceptible to hydrogen pickup under conditions conducive to cathodic charging. Anomalous results in Table IV are primarily attributed to the occasional difficulty in maintaining coupon-spacer electrical contact.

Figure 10 is a photomicrograph of one of the coupons, machined from a process tube and without any additional surface treatment, exposed in an aluminum holder. This particular coupon was exposed in the downstream portion of tube 3878-KW for 247 operating days. As shown in Figure 10, hydriding appeared to be more uniform on the OD of the coupons than on the ID. Analysis of material immediately adjacent to that shown in Figure 10 resulted in a value for total hydrogen concentration of 243 ppm. Analysis after etching material from both the ID and OD of the coupon revealed a base metal concentration of 55 ppm. Total and base metal concentrations of punchings from a second coupon exposed in the same holder were 202 and 51 ppm, respectively. As indicated in Table IV, hydrogen concentration of process tube materials prior to exposure was less than 10 ppm.

A second pair of coupons was exposed in a tube adjacent (3877-KW) to the one discussed in the preceding paragraph. These particular coupons attained 106 days of operating exposure in an aluminum holder prior to discharge. Total hydrogen concentrations of the two coupons, 154 and 274 ppm, were not strikingly different from that found in the two coupons with the 247 days of exposure. Base metal concentrations of the two coupons with the shorter exposure were 31 and 33 ppm. This compares to the values of 51 and 55 ppm previously presented for the coupons with the longer exposure.

Spacer Tests. This section of the report, a summary of information presented in References 5 and 19, compares the effects of charging reactor process tubes with special "cathodic" and anodized aluminum spacers to those arising from the use of the standard 6063 aluminum spacer-tube

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FIGURE 10. Hydride Formation Resulting From In-Reactor Coupon Exposure

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combination. Stainless steel and nickel plated aluminum spacers were exposed to investigate the effect of reversing the polarity of any electrochemical cell arising from galvanic contact. Anodized aluminum spacers were charged to investigate the effect of insulating the spacers from the tube walls, the insulation being the oxide coating. All of the special spacers were exposed in "new" process tubes, those which replaced hydrided tubes removed to investigate the extent of attack. The new or unhydrided tubes and the variety of special spacers permitted additional investigation of both remedial measures and the validity of electrochemical mechanism.

Two of the replacement tubes, one containing nickel plated spacers and one containing stainless steel spacers, were examined after 4 mo of exposure. Hydrogen concentrations found in the two tubes are shown in Figure 11 along with those found in a new replacement tube, which had been equipped with standard spacers, with comparable exposure. Except for the downstream 8 to 9 in. of tube 3667-KW2, tubes containing the special "cathodic" spacers had hydrogen concentrations of only 8 to 15 ppm, suggesting that no hydriding had occurred. This is in obvious contrast to the effects of the exposure of the tube with a standard aluminum spacers. The hydride found in the downstream 8 to 9 in. of tube 3667-KW2 was apparently the result of inadvertently charging unplated instead of nickel plated spacers in the first two spacers positions. ⁽⁵⁾

Two other replacement tubes, one containing anodized spacers and a second tube charged with nickel plated spacers, were examined after attaining 6 mo of exposure. Extensive examination indicated that no hydriding occurred. Maximum concentrations found in the tubes with anodized aluminum and nickel plated aluminum spacers were 12 and 14 ppm, respectively. The lack of hydriding associated with the special spacers was verified by metallographic examination. ⁽¹⁹⁾

The nickel plated spacers were significantly corroded. For the most part, corrosion attack appeared to be limited to the nickel plate and, except where the plate was broken, terminated at the first

FIGURE 11. Hydrogen Concentration of Tubes Charged with Special Spacers

[REDACTED]

nickel-aluminum diffusion layer. Examination of the stainless steel spacers revealed no evidence of pitting or corrosion. The aluminum tube-nozzle gasket associated with the tube containing stainless steel spacers was, however, very badly pitted. As stated in Reference 19, "The anodized aluminum spacers were given a one mil coating in oxalic acid and sealed for 2 hours in 170 °C deionized water. Examination showed virtually no corrosion initiated by reactor environment. There was some light abrasion damage along the edges of the ribs, resulting in slight aluminum corrosion at the scratches..."

Remarks Concerning Mechanism

There is no intent to imply that all of the potential causes that were proposed at one time or another have been discussed. Hydrogen pickup arising from the aqueous corrosion of Zircaloy-2 should be, at least, mentioned. This potential cause was dismissed at an early date since introduction of the amounts of hydrogen actually found would require extensive process tube corrosion. It was calculated that introduction of 1000 ppm of hydrogen into the tubes would require formation of at least a 0.003 in. thick layer of corrosion product (zirconium oxide).⁽²⁾ Examination of tubes has revealed no evidence of corrosion product anywhere near this order of magnitude. A 0.003 in. thick oxide film corresponds to a corrosion product deposit (weight gain) greater than 1500 mg/dm². As indicated earlier, measured weight gain is less than 1 mg/dm², even after 47 mo.

Consideration of the electric potential generated by flow, the streaming potential, led to another postulated mechanism. As reported in Reference 20, "the tube wall will be cathodic to part of the fuel element surfaces. If there is good electrical contact between the fuel elements and the tube. . . then hydrogen could be liberated at the tube walls. This could then cause hydrogen embrittlement. . . or any one of the other possible problems caused by cathodic hydrogen evolution." There is no experimental evidence to link the tube hydriding phenomenon with streaming potential.

[REDACTED]

[REDACTED]

Process water quality should also be mentioned before ending any discussion of possible causes. At first, water quality was discussed in relation to radiolytic hydrogen production or hydriding arising from the formation of crud films. Out-of-reactor tests resulting in hydride formation proved that radiation was not a necessary catalyst. No evidence was found to establish that crud formation was a prerequisite to hydriding. As it became apparent that hydride formation was an electrochemical process, process water again came under consideration, this time as an electrolyte. It is known that small concentrations of certain impurities can significantly effect hydrogen entry during the cathodic charging of hydrogen into steel. ^(13, 21) It was felt that one or more of the constituents of process water, like certain impurities in the case of steel, might promote the hydriding of zirconium. Investigation of the effect of changing dichromate concentration shows that this particular ion acts as a catalyst. Attempts to quantitatively evaluate the effect have product scattered results. Work related to this particular area is continuing but it may not be possible to remove or change the concentration of a particular process water constituent, even though proof is obtained that the constituent significantly affects the rate of hydriding. A change in concentration, although reducing the rate of hydriding, might at the same time result in deleterious effects on corrosion rate or effluent activity.

It has been stated several times that most of the hydriding has occurred in the portions of the tubes where spacers are located. It is of interest to note that review, although revealing no positive reason for the preceding observation, suggested that protective zirconium and aluminum oxide films may be at least part of the reason why hydride was usually not found in the portion of tubes where fuel elements are located. The fact that fuel elements are clad with aluminum alloy type 8001 may also be part of the reason, since tests have suggested that hydriding arising from a Zircaloy-6063 Al galvanic couple is more extensive than that arising from a Zircaloy-8001 Al couple.

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Examination of tubes as well as out-of-reactor tests has indicated that relatively thick hydride case layers can be formed quickly, (in a matter of weeks). In most instances, the rate of case-layer growth must fall off fairly rapidly or even thicker cases would have been observed. At this time, it is of interest to note that diffusion of hydrogen through zirconium hydride was suggested as a rate limiting mechanism for case formation in one of the earliest investigations of cathodic charging by an applied potential.⁽¹⁴⁾ For current densities greater than 100 mA/cm^2 , case thickness was quantitatively related to the square root of the product of the diffusion coefficient and time.

In contrast to the rate of case layer growth, it appears that the rate of increase of base metal hydrogen concentration is almost linear, always at a very low value. Several months of exposure are apparently needed to observe changes in base metal concentration. The term supercharging is frequently used when discussing the buildup of hydrogen in the base metal, despite the low rate of increase. This is because the base metal concentrations found are obviously higher than the values reported for terminal solid solubility of hydrogen in alpha zirconium at temperature corresponding to reactor cooling water temperatures.⁽²²⁾ The recent indication that higher base metal concentrations are associated with the thinnest portion of tube walls suggests a fairly uniform flux of active species traversing the tube wall.

Successful demonstration of remedial measures not only suggested methods for countering the attack but assisted in confirming that conditions conducive to hydriding had been correctly defined. Replacement of aluminum with materials cathodic to Zircaloy-2 stopped hydrogen entry into the tube in almost every instance. Hydriding of a tube containing nickel plated aluminum spacers was subsequently attributed to the inadvertent use of unplated spacers in two of the twelve spacer positions. In tests to evaluate the effectiveness of preventing galvanic contact with

oxide films, no hydriding was found in a tube charged with anodized aluminum spacers after 6 mo of exposure. In coupon tests, metallography revealed that autoclaving Zircaloy-2 prevented uniform case hydriding but local attack did occur at imperfections or breaks in the oxide film.

Corrosion currents arising from spacer-process tube contact have been measured by Douglas United Nuclear personnel. Measuring techniques and data are presented in Reference 23. This particular investigation revealed a significant temperature effect. It was noted in Reference 23 that. . . "galvanic cell current dropped to approximately zero value six minutes after reactor scram [automatic shutdown]." The fact that even operating temperatures are relatively low may also be significant because of the associated inability to form protective zirconium oxide films on tubes originally installed in the bright condition. Additional investigation of the effect of temperature on the cathodic charging of hydrogen into Zircaloy is needed.

In summary, there is no complete theory concerning the hydriding of process tubes. Investigation of possible mechanisms, however, has consistently shown that in low temperature process water, the galvanic couple formed by aluminum and zirconium alloys can result in hydrogen pickup in the zirconium alloy, the cathode of the couple. This cathodic charging of hydrogen into zirconium alloys with potentials (current densities) arising from a galvanic couple has been demonstrated both in-reactor and out-of-reactor.

REDISTRIBUTION OF THE HYDRIDE CASE^(6, 18)

It appears hydride formation can be arrested by relatively conventional techniques. The case that has formed obviously has affected physical properties (e. g. , ductility and impact strength have been reduced), but should not cause process tube failure.^(24, 25) On the other hand, hydrogen migration from the dense case on the inner surface of the tube into underlying material could result in additional changes in physical properties even

after further hydrogen absorption attack is stopped. A detailed review revealed no known mechanism which could bring about such a hydrogen redistribution but it was felt that because of potential detrimental effects, investigation of the effect of continued exposure on existing hydride distributions, especially under conditions not conducive to hydriding, was justified.

Test Program Techniques

The test program to investigate the effects of exposure on existing hydride distributions utilized one of the techniques previously described—coupon exposure. In this instance, coupons were machined from the downstream 5 ft of two process tubes that had been previously installed in-reactor. The coupons were, therefore, prehydrided, having a case of hydride platelets on the coupon ID as well as base metal concentrations significantly higher than material with no in-reactor exposure. The coupons were machined from tubes 3181-KE and 3966-KW that had been installed from October, 1963, to October, 1965, and from November, 1963, to December, 1965, respectively.

Machining resulted in coupons about 1 in. long and 1 in. wide. The coupons were then loaded into either aluminum (Type 6063) or stainless steel (Type 304) holders. As in the case of previously described coupon tests, the two types of holders permitted investigation under conditions conducive as well as not conducive to hydriding. Coupon dimensions were selected that would provide a tight or forced fit between coupons and holders. Three aluminum and three stainless steel holders were fitted with coupons. Each of the six holders was equipped with six hydrided coupons from tube 3181-KE and six coupons from tube 3966-KW, along with two control coupons, i. e., coupons machined from a Zircaloy-2 process tube with no in-reactor service. The six assembled coupon holders were then charged into KW Reactor. Process tubes 3877-KW, 3878-KW, and 3879-KW were each charged with one aluminum and one stainless steel holder at spacer positions 3 and 5 (near the downstream end of the tube).

Material immediately adjacent to locations where coupons were machined from tubes, termed side strips, was retained (see Figure 2). This allowed the comparison of the hydrogen content of material with no additional exposure, the side strips, to that of material with additional exposure, the coupons.

Test Results

To date, two sets of coupon holders (one set consists of one aluminum and one SS holder) have been discharged from KW Reactor. The first and second set of holders attained 106 and 247 operating days of exposure, respectively. The electrical resistance between each coupon and its holder was measured before disassembly. Measurements indicate that except for one of the coupons of the aluminum holder of the second set of holders, galvanic contact was retained during exposure. Results of the analyses of the control coupons (material without any previous exposure) will be reviewed before discussing the effects of additional exposure on the hydrided coupons.

Analyses of Control Coupons

Results of the analyses of control coupons were previously presented as part of the information of Table IV (see data for tubes 3877-KW and 3878-KW). In summary, analyses of base metal concentration confirmed that conditions conducive and not conducive to hydriding existed in aluminum and stainless steel holders, respectively. As was indicated in an earlier section, base metal analyses of control coupons exposed in aluminum holders for 106 and 247 operating days were 31 to 33 and 51 to 55 ppm, respectively. Hydrogen content of material with no in-reactor exposure was 6 ppm, the same concentration found in all four control coupons that had been exposed in the two stainless steel holders.

Analyses of Side Strips and Prehydrided Coupons

The analyses of prehydrided coupons and side strips machined from the two previously installed process tubes are presented graphically in

Figures 12 through 15. These figures show the comparison of base metal analyses of coupons with additional exposure and side strips without additional exposure. Base metal analyses were of primary interest because a test or exposure in a stainless steel holder, resulting in an increase in concentration of metal underlying the case, would suggest migration and possible embrittlement. Two techniques were used for removing the hydride case, i. e., preparing samples for base metal analysis, machining and etching.

Analyses of Side Strips. Before proceeding, it should be noted that analyses of side strips showed that the initial two-year exposure of tubes 3181-KE and 3866-KW resulted in fairly representative hydride distributions. In fact, most of the data selected to represent the extent of attack, presented in a previous section of the report, resulted from the analyses of these tubes. Hydrogen concentrations found after removal of the case, although 10 to 20 times lower than analyses determined with the case intact, were significantly higher than concentrations associated with tube material with no in-reactor exposure. As shown in Figures 12 through 15, in general, base metal concentration decreased as distance from the downstream end of the tube increased. Values shown in these figures are arithmetic averages of from two to six base metal analyses of side strips located on both sides of a coupon and are associated with a 1 in. length of tube. The distance shown on the figures is the distance from the downstream end of the tube to the center of the side strip. (Analyses of side strips shown in Figures 12 and 14 were previously presented in Figure 5.)

Analyses of Coupons Exposed for 106 Days. Base metal analyses of coupons machined from the two process tubes and then exposed for 106 operating days are shown as individual data points in Figures 12 and 13. About 80% of the 93 analyses associated with coupons exposed in the stainless steel holder, approximate the base metal hydrogen concentration of

FIGURE 12. Hydrogen Concentration of Coupons From Tube 3181-KE, 106 Day Exposure

FIGURE 13. Hydrogen Concentration of Coupons From Tube 3966-KW, 106 Day Exposure

FIGURE 14. Hydrogen Concentration of Coupons From Tube 3181-KE, 247 Day Exposure

FIGURE 15. Hydrogen Concentration of Coupons From Tube 3966-KW, 247 Day Exposure

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the side strips. These analyses suggest that additional exposure resulted in no obvious significant increase in hydrogen concentration, i. e., no migration occurred. The specific reason for the 10 to 12 analyses which suggest an increase is unknown. Attempts to reproduce these contradictory hydrogen analyses were unsuccessful.

In general, for coupons exposed in the aluminum holder, base metal analyses which were determined after machining the case from the coupon, indicated that the concentration of underlying material had increased. Base metal analyses associated with etched coupons, however, were inconclusive. Only the base metal analyses of coupons from the two tubes that were exposed in the aluminum holder and then etched are shown in Figures 12 and 13. Although some of the analyses suggest higher hydrogen concentrations, many simply approximate those established by analyses of coupons from the stainless steel holder and the side strips. The fact that the analyses of etched coupons sometimes suggested no change, while those of machined coupons usually indicated an increase in base metal concentration is partially attributed to the method of sample preparation. When the case was etched from the ID of coupons, about 0.002 in. was also etched from the coupon OD. Nothing was removed from the OD of coupons when the case was machined from the ID. The ID of the coupon was case-hydrided because of the two-year tube exposure, but it must be remembered that the additional 106 day exposure was the first contact of OD material with hydriding conditions. Metallography revealed no obvious case formation on the OD of the pre-hydrided coupons that were exposed in the aluminum holder but repeated higher analyses associated with machined coupons indicates that concentrations near the OD must have been higher than that of the base metal.

The fact that increases in base metal concentration were not always observed in coupons exposed in the aluminum holder (i. e., under conditions conducive to attack) was primarily attributed to a low rate of

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hydriding in the material underlying the case. The first set of holders simply were not subjected to sufficient additional exposure under conditions conducive to hydriding to result in observable increases in base metal concentration.

Analyses of Coupons Exposed for 247 Days. Base Metal analyses of coupons exposed for 247 operating days are shown in Figures 14 and 15. Review of these figures will reveal that analyses of coupons from the second set of holders again indicate that exposure in the stainless steel holder resulted in no change in base metal concentration. Exposure under conditions that do not promote cathodic charging apparently results in no hydrogen migration from the case into underlying material.

In contrast to earlier results, analyses of coupons that had been exposed in the aluminum holder almost always resulted in values obviously higher than those previously established by the analyses of side strips.* As shown in Figure 15, the lack of an increase in hydrogen for one coupon exposed in an aluminum holder can probably be explained by the loss of galvanic contact sometime during the exposure. The average difference in base metal hydrogen analyses between coupons exposed in the aluminum and SS holders is about 12 ppm.

Remarks Concerning Redistribution Studies

In summary, analyses of base metal concentrations revealed that apparently no redistribution of hydrogen results from exposure under conditions that do not promote cathodic charging. As indicated earlier, no mechanism could be proposed for migration from the case to underlying material in previously hydrided tubes. The preceding statement obviously assumes that the only anticipated change is from

* For coupons from the second set of holders, only etching was used as a method of preparing samples for base metal analyses. In addition to removing the case from the ID, 0.002 to 0.003 in. was also etched from the coupon OD.

conditions conducive to hydriding to those which are not conducive to hydriding. There is no intent to imply that other changes will not provide a driving force for diffusion, e.g., establishment of temperature gradients could result in hydrogen redistribution.

Comparison of the total hydrogen concentration, i. e., comparison of analyses with the case intact, of side strips and prehydrided coupons indicated that additional exposure resulted in no detectable overall change in any of the coupons. It is felt that the high total concentrations simply masked any changes that did occur. Comparison of photomicrographs of selected coupons and side strips after additional coupon exposure revealed no obvious differences.

The difference of 12 ppm found in analyses of coupons exposed in the aluminum and SS holders corresponds to a rate of increase of base metal hydrogen concentration of samples exposed in the aluminum holder of only about 1.5 ppm per operating month. It is of interest to note that this value is similar to the 2.2 ppm per month obtained by plotting maximum base metal concentration against total service time.

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APPENDIX

Thirty four tubes which had been equipped with 6063 Al spacers were examined for hydride. As indicated in the text, without exception, all were hydrided. Table A-1 presents total and base metal hydrogen concentrations found at various distances from the downstream end for 24 of the tubes. Additional data for tube 3181-KE was presented in Figures 5, 12, and 14, while additional data for tube 3966-KW was presented in Table I and Figures 13 and 15. In addition to tubes listed in Tables A-1 and II, hydride was found in the following tubes: 3679-C (57 mo service in C Reactor); 3586-D (118 mo service in D Reactor); 4167-KE (34 mo service in KE Reactor); and 8351-Ke, 5353-KE, and 5458-KE (all with 28 mo service in KE Reactor).

TABLE A-1. Hydrogen Concentration (ppm) of 24 Reactor Process Tubes

Tube Number	Length of Service (months)	Total (T) or Base Metal (B) Concentration	Distance from Downstream End of Tube (inches)																
			5 to 7	11 to 12	16 to 18	22 to 24	35 to 37	46 to 48	54 to 60	66 to 72	78 to 84	92 to 96	104 to 108	116 to 120	128 to 132	140 to 144	152 to 156	166 to 168	178 to 180
4372-KE3 ⁽⁵⁾	4	T	274	132	112	98	90	59	-	73	38	29	11	9	9	8	9	-	-
3075-KW2 ⁽³⁾	4	T	525	602	-	263	-	-	234	195	12	-	11	10	12	23	12	-	12
		B	-	16	-	14	-	-	16	14	18	-	11	10	21	21	12	15	17
3074-KW2 ⁽⁴⁾	7	T	200	-	774	648	391	311	228	-	-	-	-	-	-	-	-	-	-
		B	-	-	-	22	-	-	17	-	-	-	-	-	-	-	-	-	-
3075-KW1 ^(2, 3)	20	T	-	1380	-	-	-	-	-	-	-	450	37	-	-	-	-	-	-
		B	53	-	-	51	53	-	-	-	-	-	-	-	-	-	-	-	-
2169-KE1 ⁽³⁾	22	T	296	-	-	-	-	-	-	-	-	357	-	-	-	-	-	-	-
		B	-	-	25	-	-	-	-	-	-	33	-	-	-	-	-	-	-
3667-KW1 ⁽⁴⁾	23	T	199	-	-	209	193	179	136	-	-	-	-	-	-	-	-	-	-
		B	-	-	-	54	-	-	37	-	-	-	-	-	-	-	-	-	-
3181-KE1 ^(4, 6, 18)	24	T	-	896	788	858	-	370	300	-	-	14	14	14	-	-	-	-	-
		B	-	76	67	59	57	46	35	-	-	-	-	-	-	-	-	-	-
3966-KW1 ^(4, 6, 18)	25	T	1410	1330	1030	710	410	320	300	-	-	-	-	-	-	-	-	-	-
		B	73	58	60	52	43	42	38	-	-	-	-	-	-	-	-	-	-
2048-KW1 ⁽⁴⁾	27	T	200	-	-	-	-	-	70	-	-	-	-	-	-	-	-	-	-
		B	42	-	-	-	-	-	23	-	-	-	-	-	-	-	-	-	-
5651-KW1	32	T	458	288	-	192	169	145	131	-	-	-	-	-	-	-	-	-	-
		B	27	21	-	19	15	14	14	-	-	-	-	-	-	-	-	-	-
1554-KW1	36	T	-	-	-	-	-	-	-	290	196	208	10	11	11	10	10	12	10
		B	-	-	80	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1357-KW1	40	T	934	-	-	-	-	-	-	72	73	74	8	-	8	-	-	-	-
		B	91	92	-	78	74	32	37	-	-	-	-	-	-	-	-	-	-
1773-KW1	41	T	751	437	371	224	110	98	98	52	53	63	35	19	10	7	9	-	-
		B	99	84	73	67	38	33	28	33	49	21	32	21	9	-	-	-	-
1766-KE1	41	T	512	516	445	352	220	167	167	39	47	149	13	12	13	14	14	14	15
		B	97	92	93	80	60	42	47	46	51	50	13	13	-	-	-	-	-
3172-KE1	42	T	1227	1040	654	482	273	194	124	190	80	68	29	20	10	11	11	11	12
		B	106	98	89	85	68	64	50	45	46	42	32	25	-	-	-	-	-
3160-KW1	42	T	710	827	553	637	340	208	161	-	416	72	8	-	7	8	9	10	10
		B	92	95	89	84	72	55	49	39	41	72	10	12	-	-	-	-	-
2577-KE1	43	T	422	308	247	212	139	108	91	226	329	327	93	12	11	12	11	11	11
		B	74	68	57	49	35	32	28	46	36	38	33	19	-	-	-	-	-
2571-KE1	43	T	506	239	218	213	150	131	92	144	306	248	6	5	7	7	7	6	8
		B	78	59	52	47	40	35	41	34	58	46	9	11	-	-	-	-	-
3065-KW1 ^(2, 3)	43	T	-	1210	-	630	-	790	642	-	344	-	-	-	-	-	-	-	-
		B	-	113	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1578-KW1	44	T	2480	1694	1338	1280	1317	1345	1254	-	-	682	12	11	12	11	9	10	12
		B	112	102	96	97	86	81	71	116	72	83	26	12	-	-	-	-	-
1571-KW1	44	T	1405	1366	1285	1244	877	698	605	669	581	540	407	137	10	10	10	10	13
		B	115	110	112	109	100	87	80	83	75	62	39	37	8	9	-	-	-
1960-KE1	46	B	94	83	79	75	56	52	66	57	83	88	10	-	-	-	-	-	-
1972-KE1	46	B	89	70	82	90	77	63	64	55	50	55	32	-	-	-	-	-	-
2557-KW1 ⁽³⁾	47	T	329	239	-	185	202	175	210	287	300	-	-	-	-	-	-	19	-
		B	-	100	-	85	93	78	85	94	133	27	19	-	-	-	-	19	-

* Values that are arithmetic averages of more than one analysis are underlined.

TABLE A-1. Hydrogen Concentration (ppm) of 24 Reactor Process Tubes

Tube Number	Length of Service (months)	Total (T) or Base Metal (B) Concentration	Distance from Downstream End of Tube (inches)																
			5 to 7	11 to 12	16 to 18	22 to 24	35 to 37	46 to 48	54 to 60	66 to 72	78 to 84	92 to 96	104 to 108	116 to 120	128 to 132	140 to 144	152 to 156	166 to 168	178 to 180
4372-KE3 ⁽⁵⁾	4	T	274	132	112	98	90	59	-	73	38	29	11	9	9	8	9	-	-
3075-KW2 ⁽³⁾	4	T	525	602	-	263	-	-	234	195	12	-	11	10	12	23	12	-	12
		B	-	16	-	14	-	-	16	14	18	-	11	10	21	21	12	15	17
3074-KW2 ⁽⁴⁾	7	T	200	-	774	648	391	311	228	-	-	-	-	-	-	-	-	-	-
		B	-	-	-	22	-	-	17	-	-	-	-	-	-	-	-	-	-
3075-KW1 ^(2, 3)	20	T	-	1380	-	-	-	-	-	-	-	450	37	-	-	-	-	-	-
		B	53	-	-	51	53	-	-	-	-	-	-	-	-	-	-	-	-
2169-KE1 ⁽³⁾	22	T	296	-	-	-	-	-	-	-	-	357	-	-	-	-	-	-	-
		B	-	-	25	-	-	-	-	-	-	33	-	-	-	-	-	-	-
3667-KW1 ⁽⁴⁾	23	T	199	-	-	209	193	179	136	-	-	-	-	-	-	-	-	-	-
		B	-	-	-	54	-	-	37	-	-	-	-	-	-	-	-	-	-
3181-KE1 ^(4, 6, 18)	24	T	-	896	788	858	-	370	300	-	-	14	14	14	-	-	-	-	-
		B	-	76	67	59	57	46	35	-	-	-	-	-	-	-	-	-	-
3966-KW1 ^(4, 6, 18)	25	T	1410	1330	1030	710	410	320	300	-	-	-	-	-	-	-	-	-	-
		B	73	58	60	52	46	42	38	-	-	-	-	-	-	-	-	-	-
2048-KW1 ⁽⁴⁾	27	T	200	-	-	-	-	-	70	-	-	-	-	-	-	-	-	-	-
		B	42	-	-	-	-	-	23	-	-	-	-	-	-	-	-	-	-
5651-KW1	32	T	458	288	-	192	169	145	131	-	-	-	-	-	-	-	-	-	-
		B	27	21	-	19	15	14	14	-	-	-	-	-	-	-	-	-	-
1554-KW1	36	T	-	-	-	-	-	-	-	290	196	208	10	11	11	10	10	12	10
		B	-	-	80	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1357-KW1	40	T	934	-	-	-	-	-	-	72	73	74	8	-	8	-	-	-	-
		B	91	92	-	78	74	32	37	-	-	-	-	-	-	-	-	-	-
1773-KW1	41	T	751	437	371	224	110	98	98	52	53	63	35	19	10	7	9	-	-
		B	99	84	73	67	38	33	28	33	49	21	32	21	9	-	-	-	-
1766-KE1	41	T	512	516	445	352	220	167	167	39	47	149	13	12	13	14	14	14	15
		B	97	92	93	80	60	42	47	46	51	50	13	13	-	-	-	-	-
3172-KE1	42	T	1227	1040	654	482	273	194	124	190	80	68	29	20	10	11	11	11	12
		B	106	98	89	85	68	64	50	45	46	42	32	25	-	-	-	-	-
3160-KW1	42	T	710	827	553	637	340	208	161	-	413	72	8	-	7	8	9	10	10
		B	92	95	89	84	72	55	49	39	41	72	10	12	-	-	-	-	-
2577-KE1	43	T	422	308	247	212	139	108	91	223	329	327	93	12	11	12	11	11	11
		B	74	68	57	49	35	32	28	46	36	38	33	19	-	-	-	-	-
2571-KE1	43	T	506	239	218	213	150	131	92	144	303	248	6	6	7	7	7	6	8
		B	78	59	52	47	40	35	41	34	58	43	9	11	-	-	-	-	-
3065-KW1 ^(2, 3)	43	T	-	1210	-	630	-	790	642	-	344	-	-	-	-	-	-	-	-
		B	-	113	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1578-KW1	44	T	2480	1694	1338	1280	1317	1345	1254	-	-	682	12	11	12	11	9	10	12
		B	112	102	96	97	86	81	71	116	72	63	26	12	-	-	-	-	-
1571-KW1	44	T	1405	1366	1285	1244	877	698	605	669	581	540	407	137	10	10	10	10	13
		B	115	110	112	109	100	87	80	83	75	62	39	37	8	9	-	-	-
1960-KE1	46	B	94	83	79	75	56	52	66	57	83	88	10	-	-	-	-	-	-
1972-KE1	46	B	89	70	82	90	77	63	64	55	50	55	32	-	-	-	-	-	-
2557-KW1 ⁽³⁾	47	T	329	239	-	185	202	175	210	287	300	-	-	-	-	-	-	19	-
		B	-	100	-	85	93	78	85	94	133	27	19	-	-	-	-	19	-

* Values that are arithmetic averages of more than one analysis are underlined.

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