Report No. BMI-1402

UC-25 Metallurgy and Ceramics
(TID-4500, 15th Ed.)

Contract No. W-7405-eng-92

EFFECT OF ADDITIONS TO ZIRCALOY ON HYDROGEN PICKUP DURING AQUEOUS CORROSION

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December 29, 1959

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An investigation has been conducted into the possibility of alloy additions to Zircaloy-2 to diminish hydrogen absorption during aqueous corrosion. The nickel in Zircaloy-2 is believed to be the major constituent responsible for the relatively high hydrogen absorption. Additions of up to 0.5 w/o antimony, arsenic, bismuth, or tellurium were selected on the basis of their known ability to poison the catalytic effects of nickel in hydrogenation reactions of other systems.

Results of tests conducted for a total of 224 days in 600 and 680 F water and 750 F steam revealed no decrease in hydrogen absorption in modified Zircaloy-2 containing the aforementioned alloy additions. Hydrogen absorption increased when these alloying elements were present in the range of 0.1 to 0.2 w/o. Corrosion resistance also decreased with alloy additions in these ranges.

A 2-atm partial pressure of hydrogen in the steam or above the water did not affect hydrogen absorption in the alloys appreciably. The hydrogen partial pressure did not affect time to transition in corrosion rates, but did appear to produce higher weight gains than degassed water.

INTRODUCTION

In recent years there have been reports of fuel-element failures in pressurized-water reactors in which considerable quantities of hydride were present in the Zircaloy-2 cladding.[1]* In several instances there were indications that the hydriding may have occurred before the fuel-element rupture. This suggested that there are sources of the hydrogen other than the corrosion reaction.

In a reactor operating under normal conditions there are several potential sources of hydrogen. They include:

(1) Molecular hydrogen from (a) the hydrogen overpressure employed to minimize corrosion-product (crud) deposition from ferrous components, (b) corrosion of reactor components, (c) radiolytic decomposition of water.

(2) Atomic or ionic hydrogen produced (a) at the oxide film during the corrosion of Zircaloy or (b) from the radiolytic decomposition of water.

A theory has been proposed to explain the hydriding of Zircaloy cladding on PWR-type fuel elements during reactor operation.[2] The explanation assumes that a defect occurs in the cladding, and, because of the pressure differential, water is forced into the space between the cladding and the UO_2 cores. The water then flashes to steam and its pressure equilibrates with that of the coolant water. The steam then oxidizes the

*References at end of text.

internal surfaces, and hydrogen is produced from the reaction. The hydrogen does not escape readily because of the small opening in the defect through which it must pass. The hydrogen concentration builds up, particularly in areas which are remote from the defect. The hydrogen concentration eventually becomes sufficiently high (hydrogen 10^5 times greater than steam) to cause hydrogen pickup at hot interior surface of the Zircaloy-2. Because of the thermal gradient which exists, the hydrogen then diffuses to the cold external surface of the cladding. It exceeds its solubility limit in the colder portion, precipitates as needles, and embrittles the cladding. The embrittled area finally fails by cracking and/or corrosion.

Programs to study the factors which influence hydrogen absorption during corrosion are being conducted at Argonne National Laboratory, Battelle Memorial Institute, Bettis Atomic Power Division of Westinghouse Electric Corporation, Hanford Atomic Products Operation and Knolls Atomic Power Laboratory of the General Electric Company, and Oak Ridge National Laboratory. Among other things these studies have included the following factors:

(1) The relationship of the following to hydrogen pickup:
   (a) Length of exposure
   (b) pH
   (c) Irradiation and proton recoil
   (d) Stress and strain
   (e) Alloy additions
   (f) Hydrogen content of the Zircaloy
   (g) Surface hydrides
   (h) Dissolved hydrogen in the water
   (i) Steam in molecular hydrogen

(2) The relationship of the following to hydrogen redistribution:
   (a) Heat of transport
   (b) Isothermal diffusion coefficients
   (c) Stress and strain

(3) The habit planes of zirconium hydride in zirconium

(4) The effects of hydrogen on the mechanical properties of Zircaloy-2.

A previous study at Battelle has indicated, that, under isothermal conditions in the absence of irradiation, (1) hydrogen is absorbed from the corrosion reaction on the surface of zirconium, (2) nickel contents as low as 0.06 w/o increase hydrogen absorption significantly, and (3) antimony additions in sponge zirconium reduce hydrogen absorption during corrosion.[3] Thus it appears that, to reduce hydrogen absorption in Zircaloy-2 during corrosion, (1) the nickel (about 0.05 w/o) should be removed from the alloy, or (2) a suitable alloying agent should be added which would neutralize the effect of nickel. A program to remove the nickel from Zircaloy-2 is well along at the Bettis Laboratory.[4,5] The second approach, that of alloying to overcome the adverse effects of nickel, is the subject of the present research.

The effect of nickel on hydrogen absorption in zirconium may be related to the low hydrogen overvoltage of nickel. It is known that during the electrolytic decomposition of an aqueous solution very little polarization occurs with nickel electrodes. The voltage

required to discharge hydrogen is only slightly higher than the theoretical voltage required for decomposition of the solution. Nickel, and the platinum elements, which possess low hydrogen overvoltage, also are capable of the reverse reaction of breaking down molecular hydrogen to atomic hydrogen. In this respect they are well known for their use as catalysts in hydrogenation reactions. It is possible that the nickel compounds in zirconium also may be acting as catalysts to promote hydrogen absorption. On the other hand, antimony compounds in zirconium probably have high overvoltage and do not act as catalysts.

Sulfur and similar elements such as arsenic, antimony, bismuth, and tellurium are known to poison the catalytic effects of nickel in chemical reactions. The presence of these elements also tends to affect hydrogen deposition at the cathodes of corrosion cells. A similar poisoning effect might be expected if nickel were acting as a catalyst in promoting hydrogen pickup during the corrosion of Zircaloy-2. Based on this line of reasoning, and the observed beneficial effects of anitmony in sponge zirconium, alloys were prepared containing antimony, arsenic, bismuth, or tellurium additions to Zircaloy-2. Antimony additions also were made to two modified Zircaloy-2 alloys, those containing only 1.0 and 0.25 w/o tin, respectively. Hydrogen absorption as a function of total corrosion was studied in exposures to high-temperature water and steam under (1) degassed conditions and (2) a small hydrogen overpressure.

EXPERIMENTAL WORK

Test Procedures

Melting and Fabrication

Alloys were prepared by consumable-electrode arc-melting techniques. A single ingot of Zircaloy-2 served as melting stock for the series of Zircaloy-2 alloys. The modified Zircaloys were prepared by adding the prescribed elements to sponge zirconium. All alloys were melted twice. The electrodes for the first melt were pressed compacts of the desired composition. The ingot from the first melt was then quartered lengthwise, and the quarters were welded end to end to provide the electrode for the second melt.

Nominal additions of 0, 0.07, 0.20, and 0.50 w/o antimony were made to the standard Zircaloy-2 and to modified Zircaloy-2-base alloys containing only 1.0 or 0.25 w/o tin. Additions of 0.15 w/o arsenic, bismuth, and tellurium also were made to Zircaloy-2. Analyses of the base heats and the major addition for other heats are presented in Table 1. All analyses were close to the nominal compositions except for the high iron in the low-tin Zircaloy-2 alloy series and the low arsenic in the Zircaloy-2-arsenic alloy.

Alloys were upset forged at 1650 F and rolled to 0.075 in. in thickness at 1600 F. The arsenic alloy cracked during forging. Several pieces were machined from the cracked ingot and were rolled at 1400 F with no difficulty.

TABLE 1. ANALYSES OF ZIRCALOY HEATS PREPARED FOR PROGRAM

Base Material	Nominal Additions, w/o	Analysis (Balance Zirconium), w/o							
		Sn	Fe	Cr	Ni	As	Sb	Bi	Te
Zircaloy-2	None	1.60	0.17	0.10	0.05	<0.001	<0.001	<0.0001	<0.02
	0.07 Sb	--	--	--	--	--	0.05	--	--
	0.20 Sb	--	--	--	--	--	0.20	--	--
	0.50 Sb	--	--	--	--	--	0.41	--	--
	0.15 As	--	--	--	--	0.03	--	--	--
	0.15 Bi	--	--	--	--	--	--	--	0.14
	0.15 Te	--	--	--	--	--	--	0.11	--
Modified Zircaloy-2 (1 w/o Sn)	None	1.05	0.12	0.10	0.03	<0.001	<0.001	<0.0001	<0.02
	0.07 Sb	--	--	--	--	--	0.05	--	--
	0.20 Sb	--	--	--	--	--	0.14	--	--
	0.50 Sb	--	--	--	--	--	0.46	--	--
Modified Zircaloy-2 (0.25 w/o Sn)	None	0.31	0.24	0.11	0.04	<0.001	<0.001	<0.0001	<0.02
	0.07 Sb	--	--	--	--	--	0.06	--	--
	0.20 Sb	--	--	--	--	--	0.17	--	--
	0.50 Sb	--	--	--	--	--	0.51	--	--

Specimen Preparation

Corrosion coupons were cut from the hot-rolled strip and were shaper finished to a rectangular cross section. Finished dimensions were approximately 2.0 by 1.0 by 0.05 in. A support hole 0.070 in. in diameter was drilled near the end of each specimen. Sample numbers were stamped with steel figures.

The specimens were degreased and then pickled 4 min in a room-temperature 45 volume per cent nitric acid (70 w/o acid) -5 volume per cent hydrofluoric acid (50 w/o acid) -50 volume per cent distilled water solution. After pickling, the specimens were transferred immediately to cold flowing tap water and were rinsed overnight. They were then rinsed in distilled water, dried, measured, rinsed in acetone, dried, and weighed preparatory to corrosion testing.

Exposure Conditions

The autoclaves and fittings used in the corrosion tests were made of AISI Type 316 stainless steel. A nonagitated 1-liter autoclave design was employed. Individual specimens were supported from Chromel A (80 w/o nickel -20 w/o chromium) wire hooks. Palladium "valves" for controlling hydrogen content were inserted in the headspace of the autoclaves. The valves were patterned after Bettis models and consisted of 10 ft of 0.040-in.-OD by 0.020-in.-ID tubing which was seal-welded at one end and wrapped into a coil. The open end of the palladium tubing extended out of the autoclave through a tubinglike fitting. A seal was made by brazing the tubing into the fitting at some distance from the heated portion of the autoclave.

Corrosion studies were conducted in 600 and 680 F water and 750 F 1500-psi steam under degassed conditions and under an externally applied partial pressure of 2 atm hydrogen. In the water tests, deionized water (specific resistivity greater than 1 megohm-cm) was boiled at least 1 hr to remove dissolved gases. It then was transferred to the test autoclave which was quickly sealed. A quantity of water sufficient to provide a 10 per cent vapor headspace at temperature was bled off at 250 F. The autoclave was then brought to the operating temperature. Cold deionized water in the amount of 10 per cent of the total volume was added to the autoclaves for the 750 F steam tests. The autoclaves were opened to vacuum pumps for 3 to 5-min periods with 5-min intervals between pumping. The autoclaves then were heated, and the excess water was bled off to give 1500-psi steam at 750 F.

Under degassed conditions, the exit of the palladium valve was connected to a vacuum pump which ran continuously. The 2 atm of hydrogen (absolute) was added by connecting the palladium valve to a reducing valve on a tank of hydrogen by means of copper tubing and compression fittings. Spot-check analysis of the 680 F water indicated 130 ml hydrogen per kg water, or about one-third that calculated for a partial pressure of 2 atm.[6] The hydrogen analysis under degassed conditions was less than 5 ml per kg, the limit of sensitivity of the method employed.

In the 600 F water tests the autoclaves were opened and the specimens were examined after total exposure times of 14, 28, and 56 days and every 28 days thereafter. Examinations in the 680 F water and 750 F steam tests were made after total exposure times of 7, 14, 28, and 56 days and every 28 days thereafter. Fresh water was added after each exposure.

Corrosion tests were conducted in quadruplicate. A specimen from each alloy was removed from test for metallographic examination and hydrogen analysis at total weight gains of approximately 25, 40, and 60 mg per dm^2 in water exposures and at 25, 40, and 70 mg per dm^2 in steam exposures.

Test Results

Corrosion Rates

Corrosion specimens were weighed at each examination period. Corrosion rates were established from the weight changes obtained. Specimens exposed to 600 F water and 750 F steam with 2 atm of hydrogen were weighed after 7, 14, and 224 days of exposure only. Thus, corrosion rates were not determined for these conditions. The corrosion behavior of the alloy specimens exposed to the other four conditions was typical of that of Zircaloy-2. Log-log plots of weight gain versus time resulted initially in straight lines with slopes approaching 0.33. The corrosion curves maintained this same slope during the entire 224 days of exposure in 600 F degassed water. In 680 F water and 750 F steam the usual transition in kinetics to a linear rate was observed after exposure times ranging from 65 to 135 days. Weight-change data that are typical of the alloys tested are presented in Figure 1.

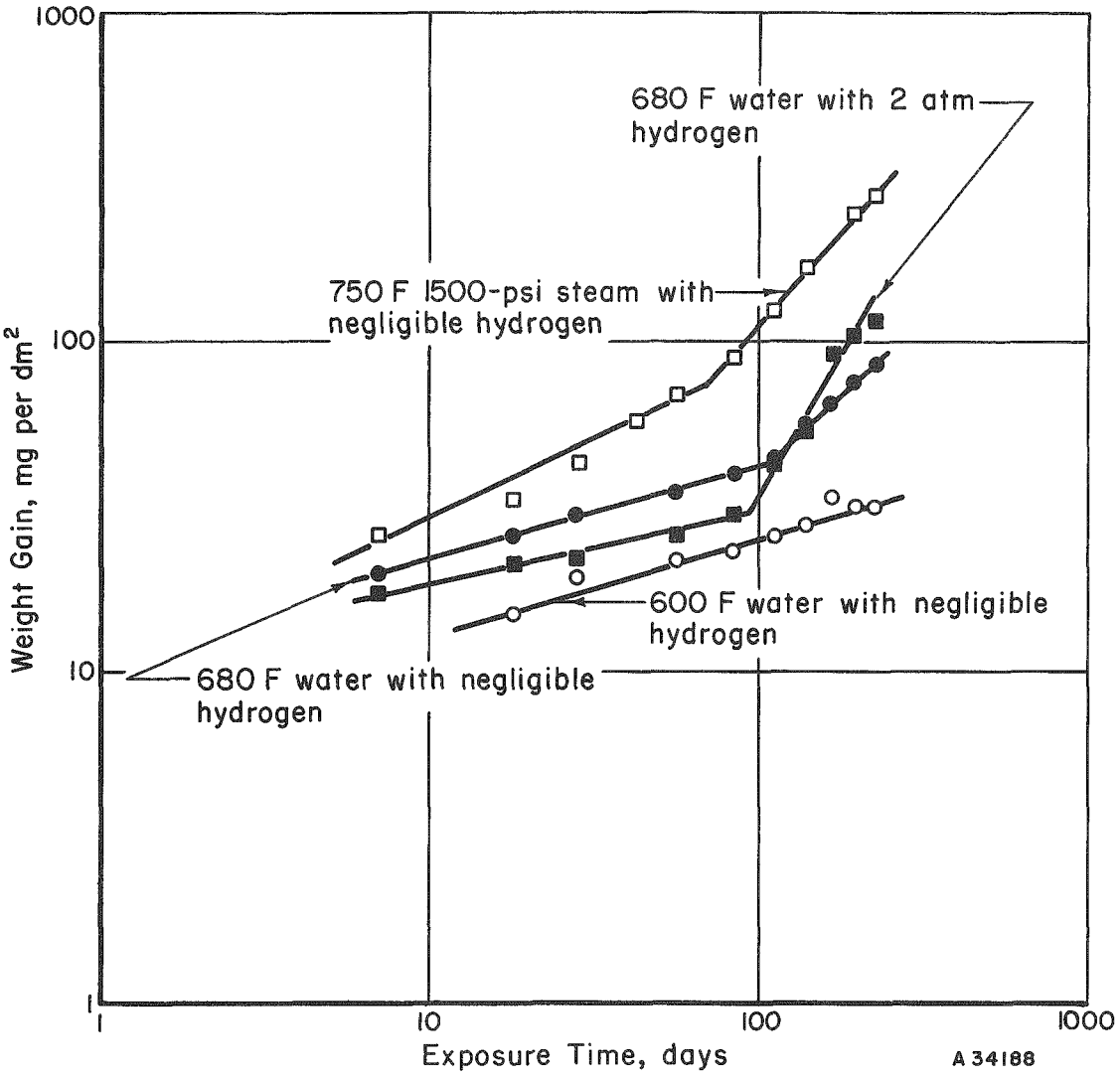

FIGURE 1. CORROSION-RATE CURVES FOR ZIRCALOY-2 WITH AN ADDITION OF 0.50 w/o ANTIMONY

The corrosion rate of the specimens can be described by the equation

$$w = kt^n,$$

where w = total weight gain in mg per dm^2, k is the 1-day intercept from the log-log plot of weight gain versus time, n is the slope of the log-log plot, and t is the exposure time in days. The constants k and n have been determined for the four test conditions where weight-gain data were recorded for the entire test period of 224 days. These are summarized in Tables A-1 through A-4 in the Appendix. Direct comparisons can be made between the 2-atm hydrogen and the degassed conditions in 680 F water only. They indicate that transition in kinetics occurs at about the same time (100 to 120 days) under both conditions. However, in general, the pretransition rate of attack was lower and the posttransition rate was higher under 2 atm of hydrogen. Comparisons at 14 and 224 days for the 600 and 750 F conditions revealed that higher weight gains were obtained with 2 atm of hydrogen.

The effect of antimony content on the corrosion behavior of the three Zircaloys is shown in Figures 2, 3, and 4. In general, antimony in the range of 0.05 to 0.5 w/o had little or no effect on corrosion behavior. A notable exception occurred in 750 F steam, where increased corrosion was observed with increasing antimony contents at 224 days of exposure (after transition).

No improvement in corrosion resistance was observed with arsenic, bismuth, or tellurium additions to the Zircaloys.

Hydrogen Absorption

The amount of hydrogen absorbed by the alloy specimens at three stages of corrosion in each of the six test conditions is presented in Tables A-5 through A-10 in the Appendix. Hydrogen analyses were obtained at weight gains of approximately 25, 40, and 60 mg per dm^2 in an attempt to compare the amounts absorbed (1) before, (2) during, and (3) after transition in reaction rates. As mentioned earlier, the alloy specimens in 600 F water and 750 F 1500-psi steam tests with 2 atm of hydrogen were examined after 7, 14, and 224 days of exposure only. Thus, a number of analyses were not obtained at 40 mg per dm^2 and the analyses of posttransition specimens in 750 F steam were made at weight gains that were much higher than 60 to 70 mg per dm^2.

In general, the amount of hydrogen absorbed varied linearly with the total amount of corrosion. However, a sufficient number of plots resulted in curves to cast some doubt on the linear relationship. Examples of both types are shown in Figure 5.

Most often, plots of hydrogen absorption versus exposure time resulted in curves similar to the corrosion curves shown in Figure 1. This was another indication of the linear relationship between total corrosion and hydrogen absorption. However, these curves were subject to some interpretation since the analyses were made at only three exposure times and hence only three points were plotted.

If hydrogen absorption is to be a criterion for the acceptance of a zirconium alloy, then the amount of hydrogen absorbed per unit of time must be known. In the present study a direct comparison could not be made at a given exposure time because analyses were made on the basis of total weight gain rather than total exposure. However, a crude comparison can be made by comparing hydrogen-absorption rates. These were

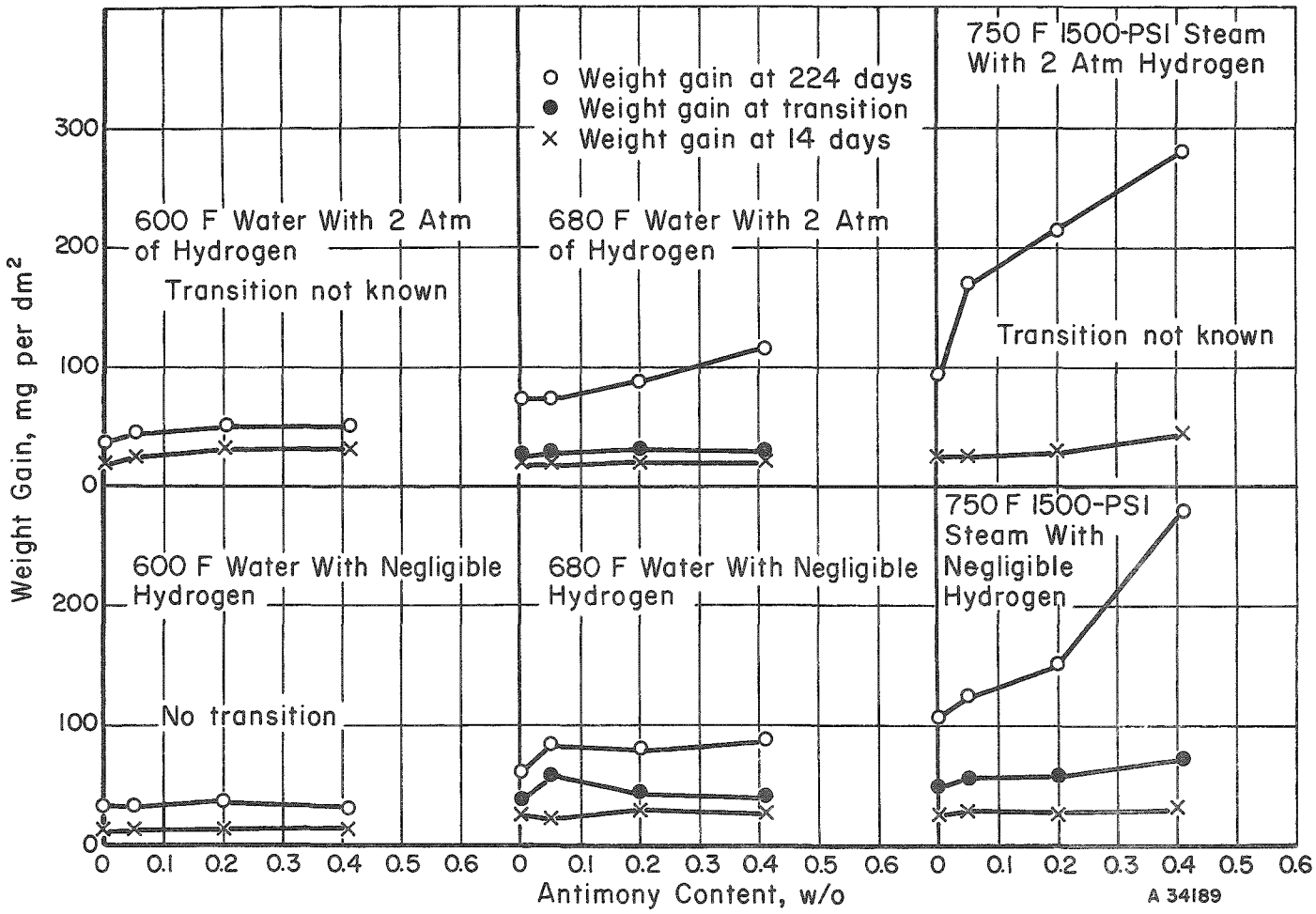

FIGURE 2. TOTAL CORROSION AS A FUNCTION OF ANTIMONY CONTENT IN ZIRCALOY-2

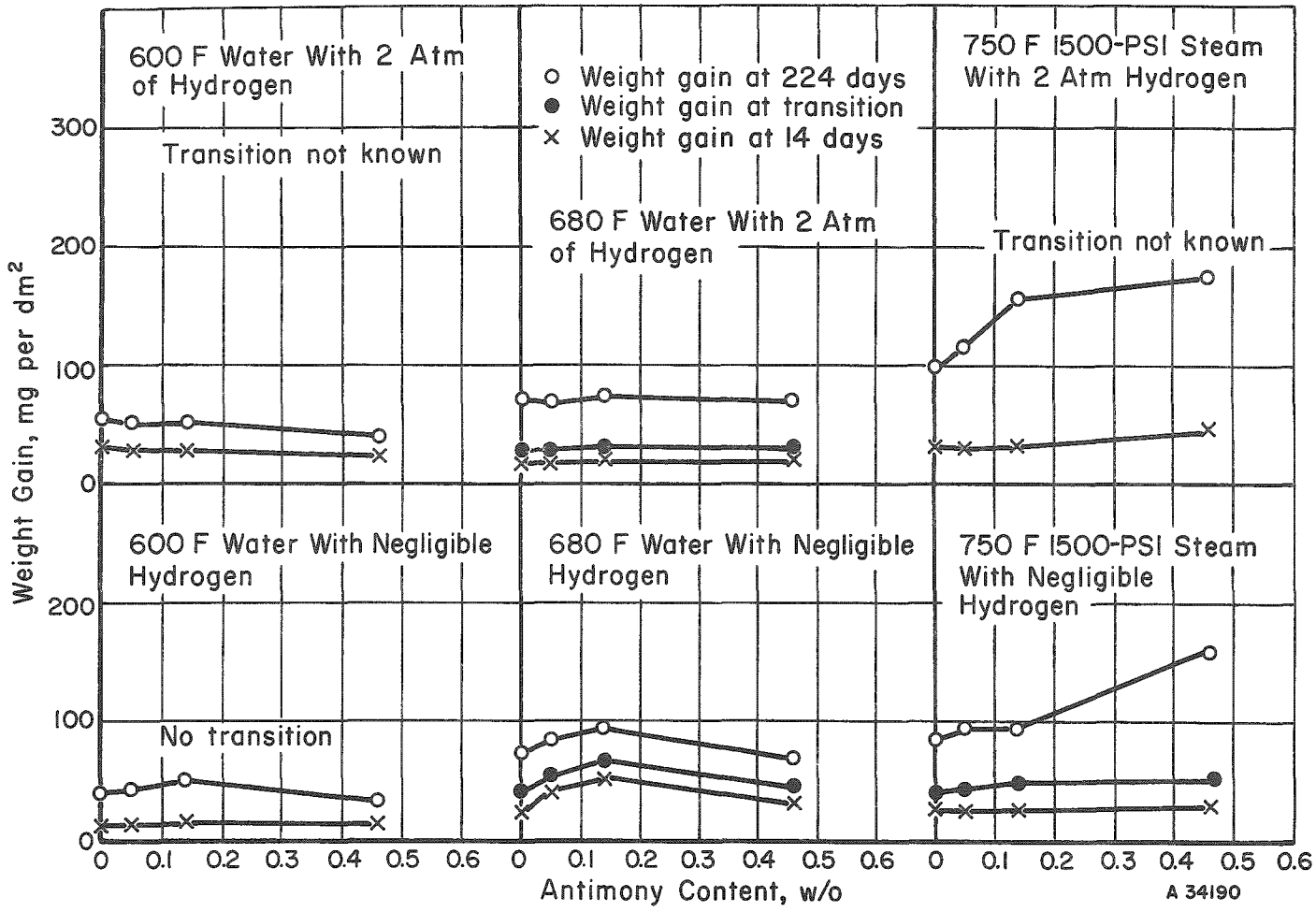

FIGURE 3. TOTAL CORROSION AS A FUNCTION OF ANTIMONY CONTENT IN MODIFIED ZIRCALOY-2 (1.05 w/o tin)

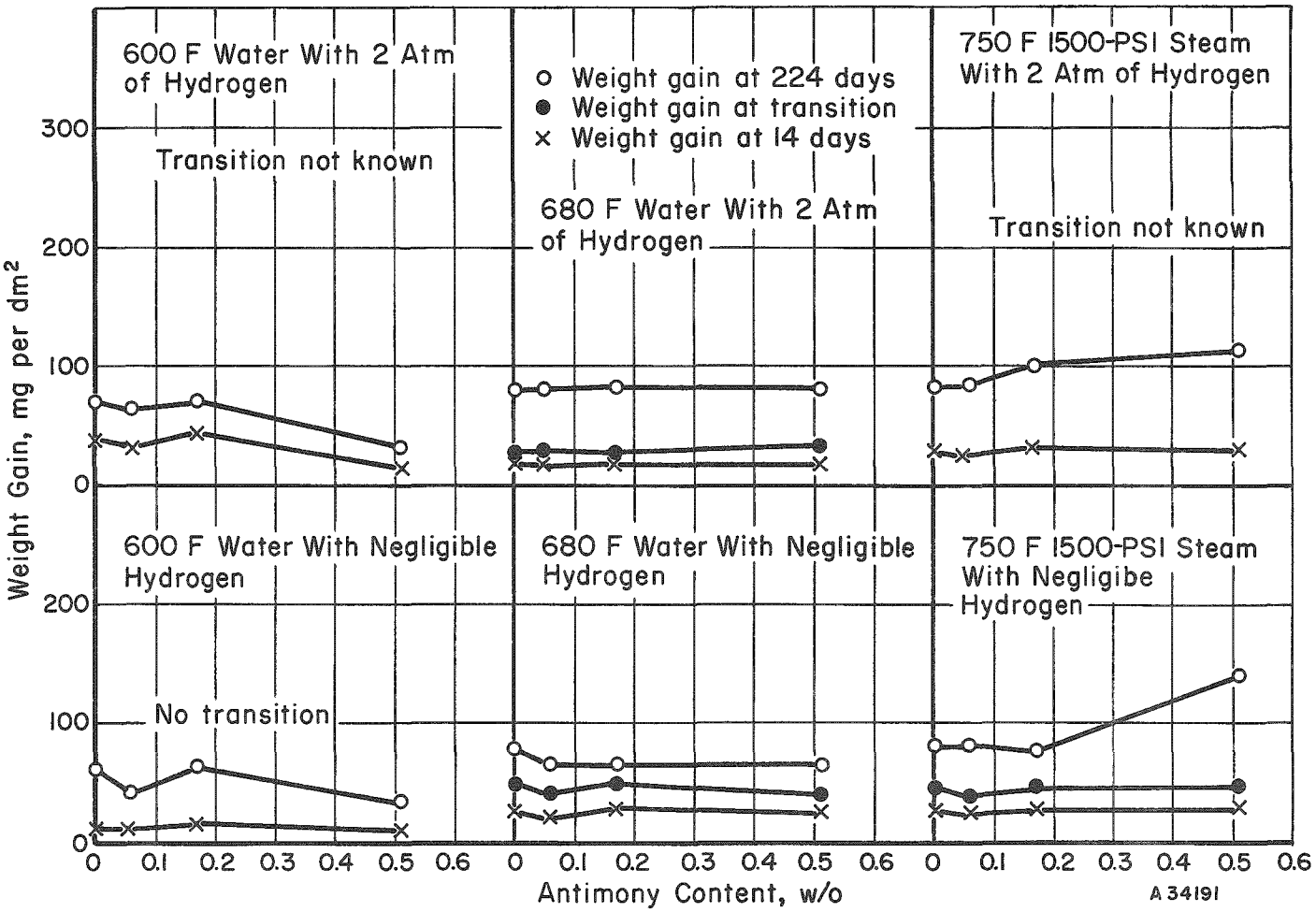

FIGURE 4. TOTAL CORROSION AS A FUNCTION OF ANTIMONY CONTENT IN MODIFIED ZIRCALOY-2 (o. 31 w/o tin)

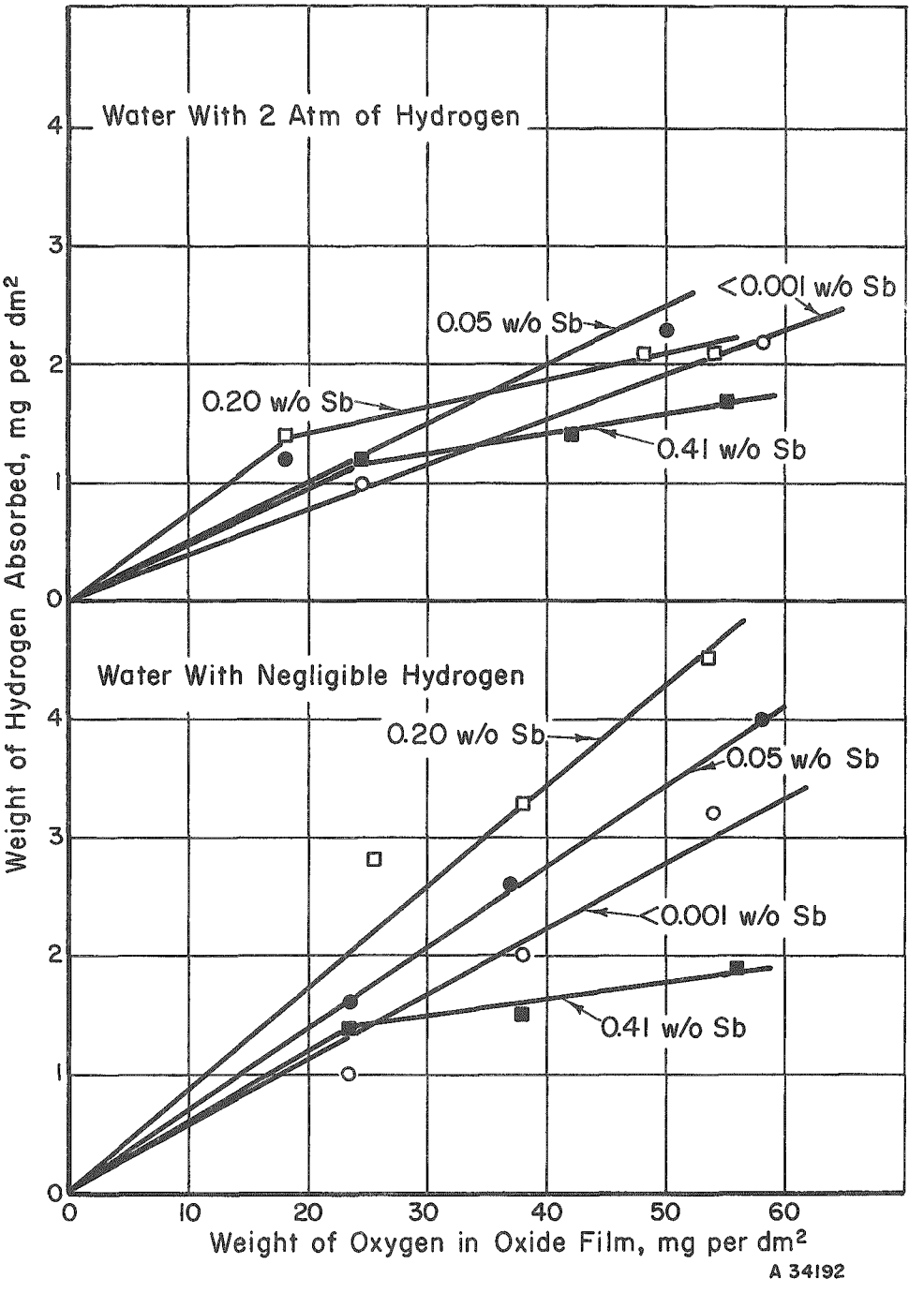

FIGURE 5. HYDROGEN ABSORPTION AS A FUNCTION OF TOTAL CORROSION IN 680 F WATER FOR ZIRCALOY-2 CONTAINING ADDITIONS OF ANTIMONY

obtained by dividing the greatest amount of hydrogen absorbed by the total exposure time and assuming that hydrogen absorption is linear with time. These results are presented in Figure 6. In general, the results indicate no beneficial effect of adding antimony to Zircaloy and a slight detrimental effect in the range of 0.2 w/o antimony. A similar effect was observed with the arsenic, bismuth, and tellurium additions. Hydrogen content of the water in the range investigated had no pronounced effect on hydrogen-absorption rate.

The ratio of hydrogen absorbed to that produced from corrosion of a given sample is expressed as a percentage of theoretical and plotted as a function of antimony in Figures 7, 8, and 9. The curves for posttransition hydrogen absorption are generally lower than those for pretransition. This suggests a nonlinear relationship between hydrogen absorption and total corrosion. However, the two curves generally are parallel and indicate that antimony additions in Zircaloy do not result in a marked reduction in hydrogen absorption. In fact, in the range of 0.1 to 0.2 w/o antimony, the percentage of theoretical absorption usually was higher than that of the base alloy or the 0.5 w/o antimony alloy. It is interesting to note from Figures 7, 8, and 9 that the modified Zircaloy-2 alloys containing 0.31 w/o tin exhibit the lowest percentages of theoretical absorption. These alloys differed from the other Zircaloys in that they were low in tin (0.31 w/o), and high in iron (0.24 w/o).

No reduction in percentage of theoretical hydrogen absorption was obtained with additions of arsenic, bismuth, or tellurium to the Zircaloys.

Metallography

Metallographic examinations were made of all alloys before corrosion testing and of selected specimens after corrosion testing. The microstructures of representative specimens are shown in Figures 10 and 11. The addition of antimony to the Zircaloys did not appear to affect the amount or distribution of the second-phase precipitate. The very small needlelike structures in the unexposed specimens containing about 0.2 w/o antimony are believed to be zirconium hydride. The unalloyed Zircaloy-2 specimen before exposure was virtually free of these small needles. Its hydrogen content was 28 ppm. At this level, the hydride which exceeds the solubility limits apparently is present as very small needles or spheroids and is difficult to distinguish from the intermetallic compounds. The absence of needles in the unexposed modified Zircaloy-2 specimen was unexpected since its hydrogen content was 70 ppm. Hydride needles are visible in normal Zircaloy-2 at this hydrogen level. Apparently the hydrogen solubility in this alloy was much higher than that in Zircaloy-2. This effect also was noted with the corrosion-tested specimens of this alloy in which the analyzed hydrogen contents were higher than one would predict from the microstructure.

For a given alloy, the amount of hydride apparent in the microstructure correlated well with the analyzed values. Similar correlations between alloys were not so consistent. An example is the small amount of hydride needles in photographs of the microstructure of the modified Zircaloy-2 specimens in Figure 11.

The large hydride needles observed after corrosion apparently are a result of growth and joining of the smaller hydride needles observed before corrosion testing. The absence of small needles in the corrosion-tested specimens points to this conclusion. For the most part, the hydride needles were not oriented in any particular direction and had the appearance of having formed at grain boundaries. However, the needles

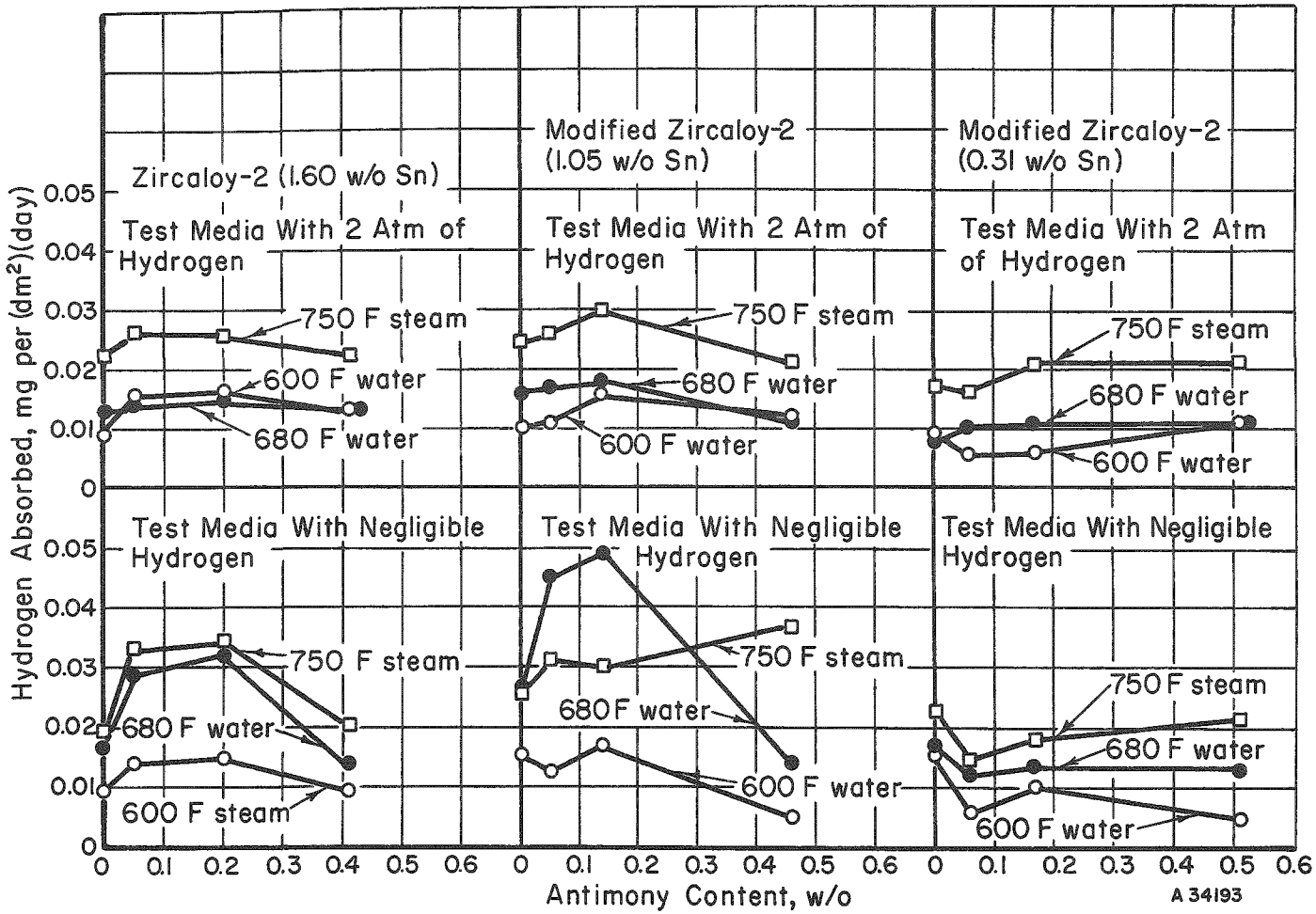

FIGURE 6. RATE OF HYDROGEN ABSORPTION DURING CORROSION AS A FUNCTION OF ANTIMONY CONTENT IN ZIRCALOY

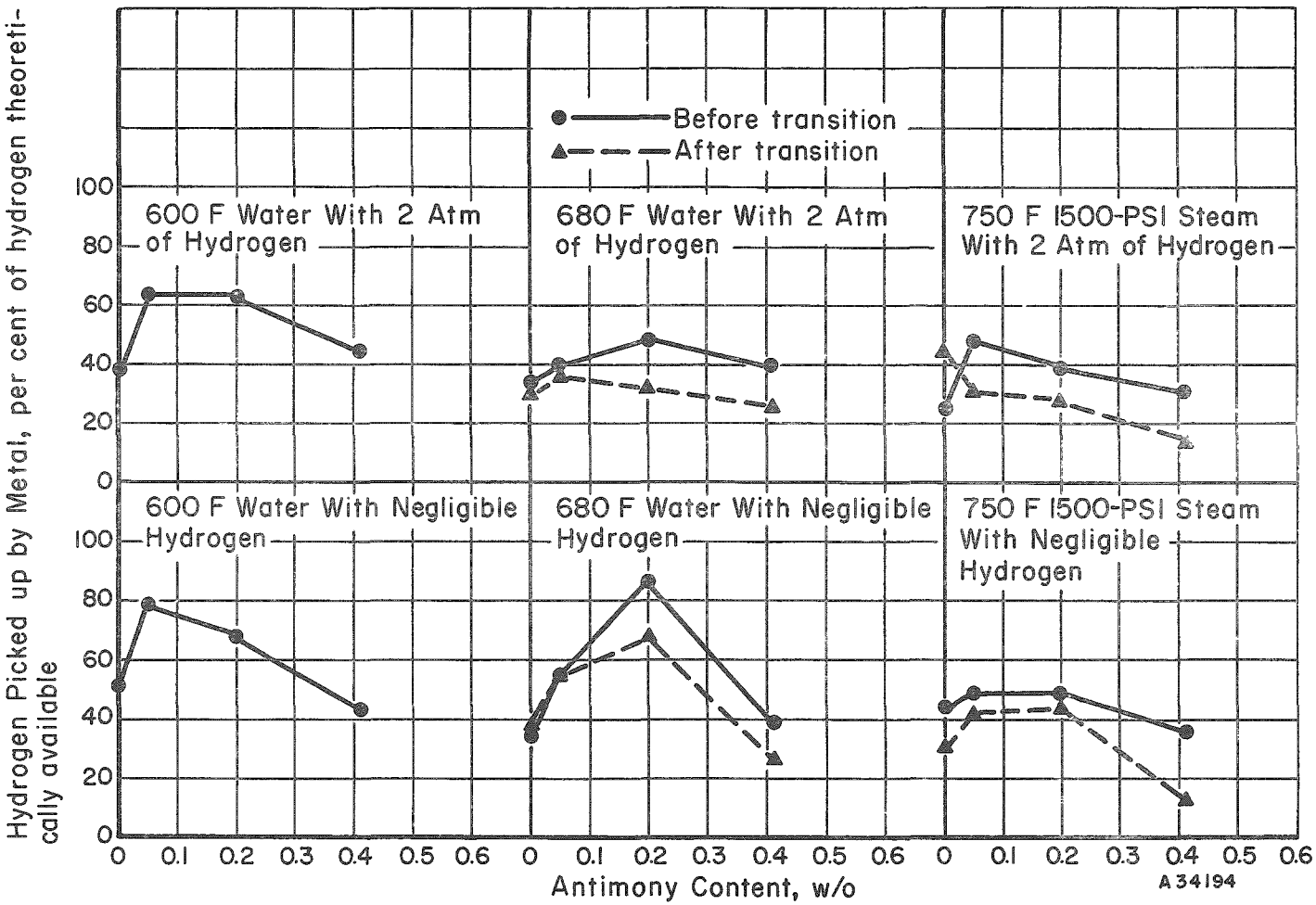

FIGURE 7. PERCENTAGE OF THEORETICALLY AVAILABLE HYDROGEN FROM CORROSION THAT IS ABSORBED IN THE METAL AS A FUNCTION OF ANTIMONY CONTENT IN ZIRCALOY-2

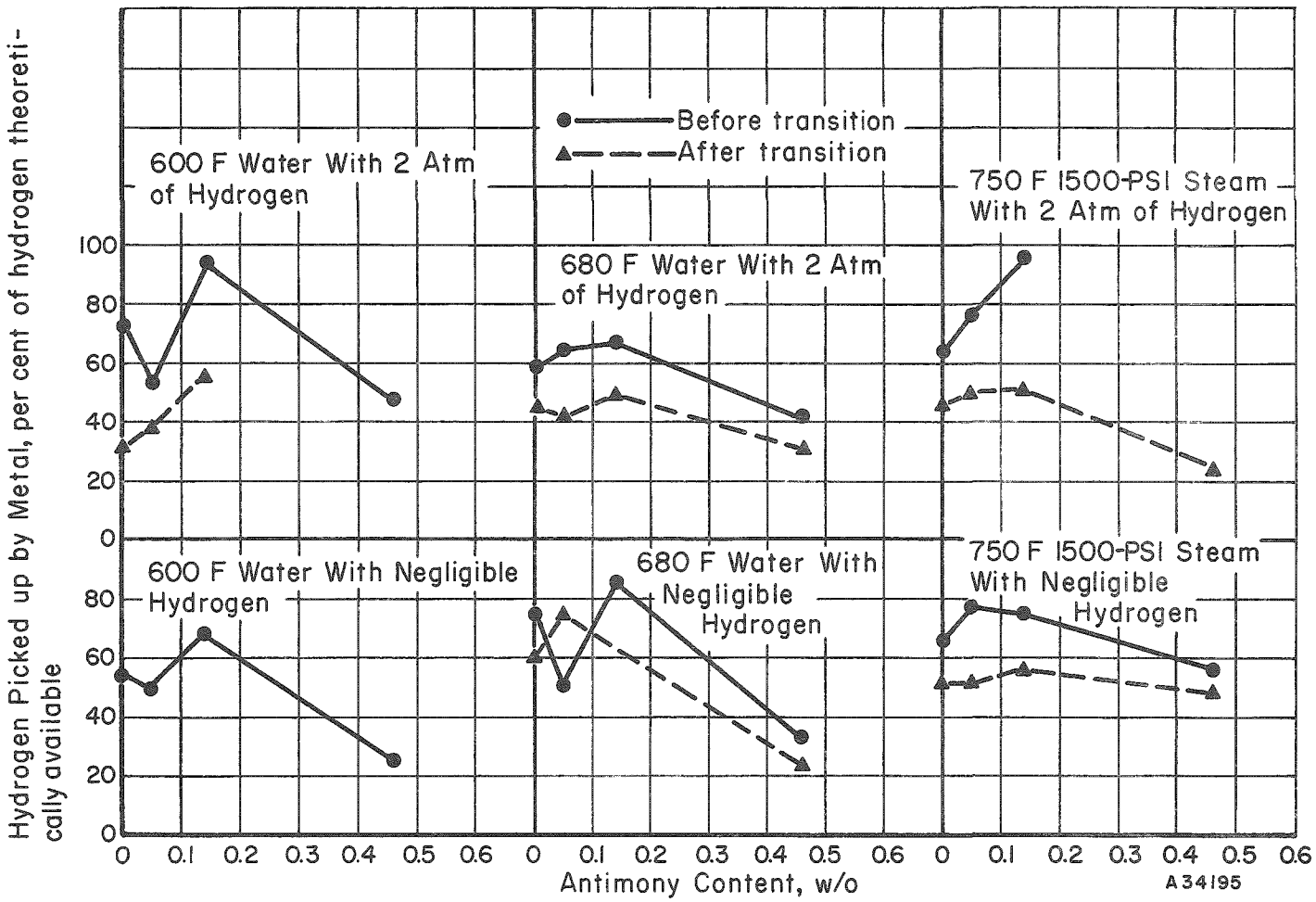

FIGURE 8. PERCENTAGE OF THEORETICALLY AVAILABLE HYDROGEN FROM CORROSION THAT IS ABSORBED IN THE METAL AS A FUNCTION OF ANTIMONY CONTENT IN MODIFIED ZIRCALOY-2 (1.05 w/o TIN)

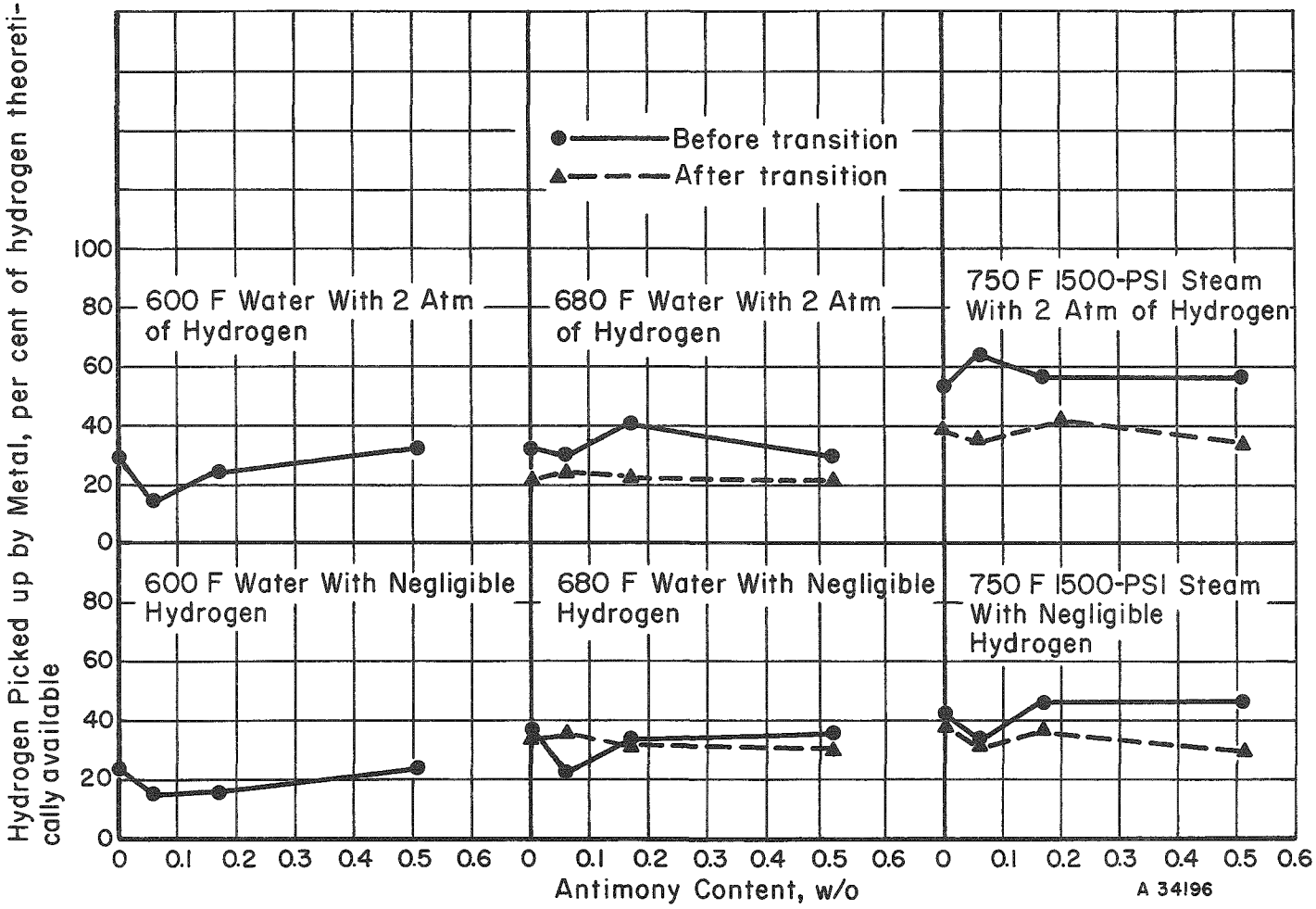

FIGURE 9. PERCENTAGE OF THEORETICALLY AVAILABLE HYDROGEN FROM CORROSION THAT IS ABSORBED IN THE METAL AS A FUNCTION OF ANTIMONY CONTENT IN MODIFIED ZIRCALOY-2 (0.31 w/o TIN)

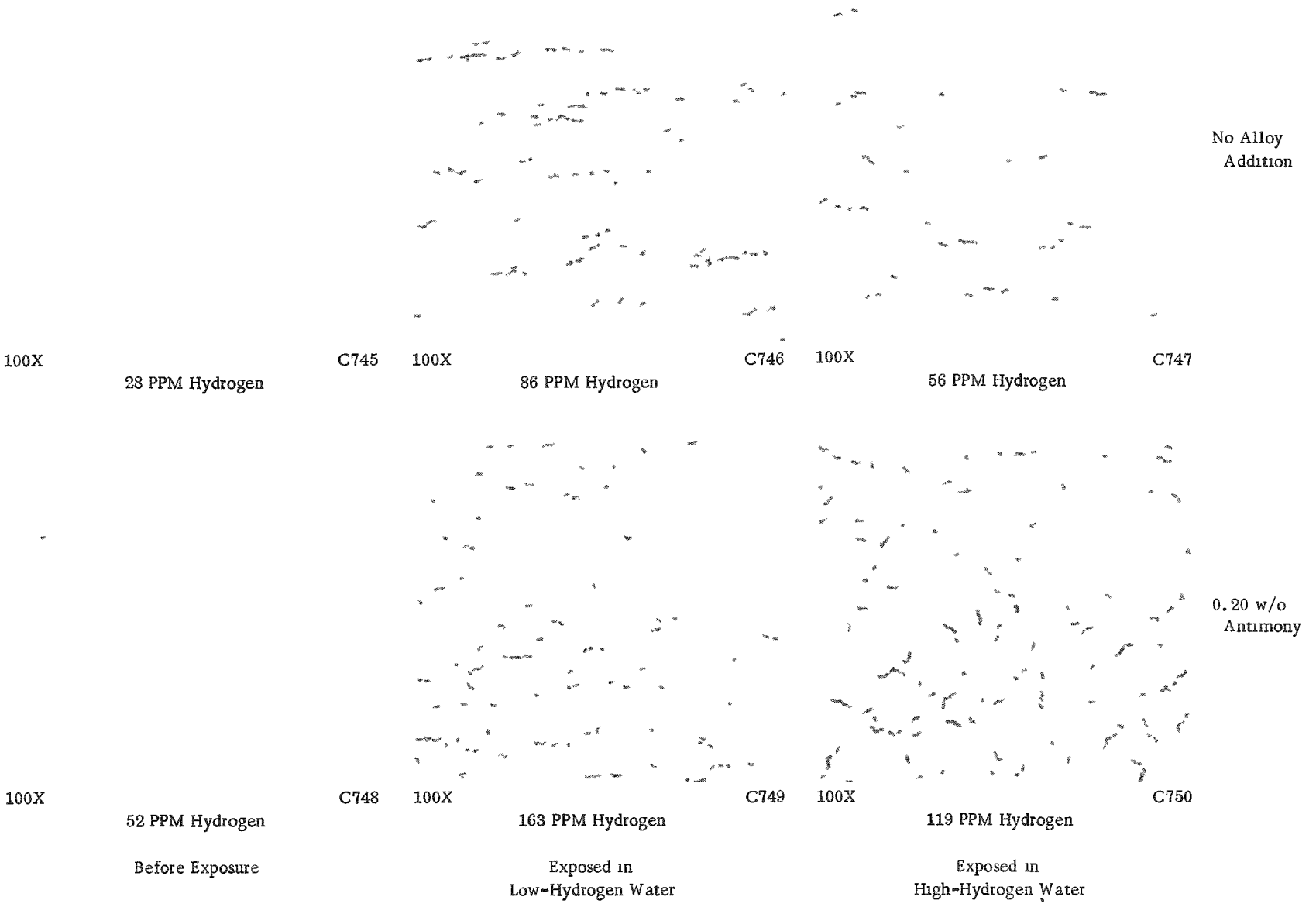

FIGURE 10. APPEARANCE OF HYDRIDE NEEDLES IN ZIRCALOY-2 WITH AN ANTIMONY ADDITION AT CORROSION WEIGHT GAINS OF 60 MG PER DM^2

Etchant. lactic-nitric-hydrofluoric acid.

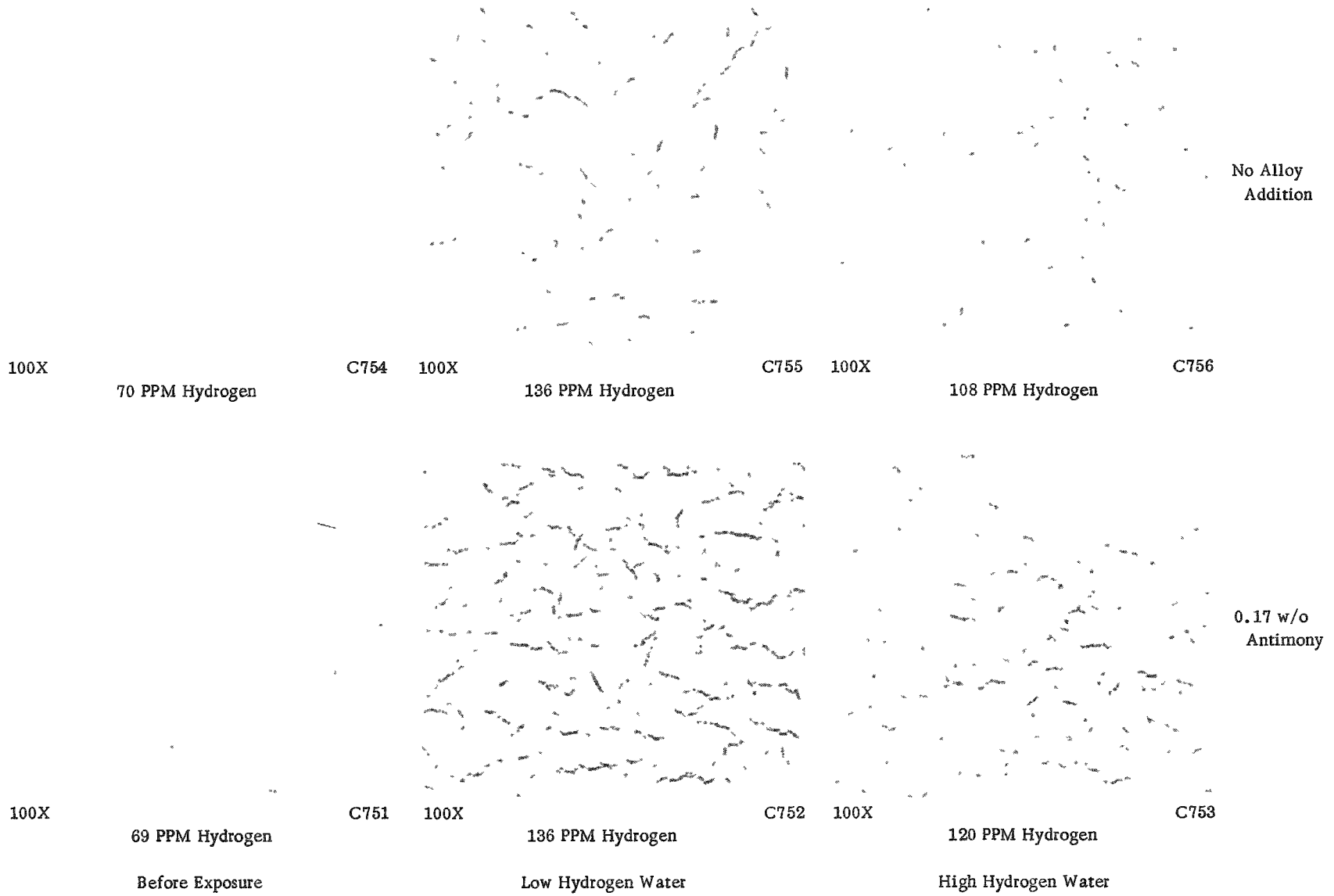

FIGURE 11. APPEARANCE OF HYDRIDE NEEDLES IN MODIFIED ZIRCALOY-2 (0.31 w/o TIN) WITH AN ANTIMONY ADDITION AT CORROSION WEIGHT GAINS OF 60 MG PER DM^2

Etchant: lactic-nitric-hydrofluoric acid.

in the Zircaloy-2 specimens were oriented more in the direction of rolling. A similar effect was observed in the Zircaloy-2 with the 0.03 w/o antimony addition. Orientation of needles in the rolling direction was observed only at the surface of the alloy specimens containing 0.14 and 0.51 w/o antimony additions to modified Zircaloy-2 (1 w/o tin).

DISCUSSION AND CONCLUSIONS

The results of the study have indicated that the addition of 0.05 to 0.50 w/o antimony or 0.15 w/o arsenic, bismuth, or tellurium to Zircaloys does not result in a marked decrease in hydrogen absorption during the corrosion of these alloys in high-temperature water. In fact, there are indications that hydrogen absorption increases slightly with additions of these elements at the level of 0.1 to 0.2 w/o. A similar effect was noted on the corrosion resistance of these alloys. Those containing about 0.2 w/o of these elements were less resistant.

Assuming that (1) nickel mainly is responsible for hydriding and (2) the aforementioned elements would poison the catalytic effect of nickel in Zircaloy-2, then it follows that nickel does not behave as a catalyst in Zircaloy to promote hydrogenation as it does in many chemical reactions.

The hydrogen overpressure employed in this study does not increase the amount of hydrogen absorbed in Zircaloys. This confirms results obtained in other studies in which partial pressures as high as 20 atm of hydrogen were investigated.[2,3] This lack of dependence of absorption on hydrogen overpressure further suggests that atomic or ionic hydrogen from the corrosion reaction is responsible for hydriding.

For the most part, the results reveal that the hydrogen-absorption rate is related directly to the corrosion rate. This indicates that, if it is assumed that all of the absorbed hydrogen comes from the corrosion reaction, the amount of hydrcgen absorbed is dependent upon the amount (concentration) of hydrogen formed on the corroding surface. Apparently, the diffusion rate through the oxide film is sufficiently rapid that it does not influence the hydrogen-absorption rate.

It is not known whether the higher weight gains obtained with Zircaloy-2 in hydrogen-containing water are an effect of hydrogen or whether they represent the scatter in results from other experimental variables. If it assumed that there is an effect of hydrogen in the water, it may be possible to explain the scatter in corrosion results. Present testing of Zircaloy-2 is usually done in large autoclaves containing many corroding surfaces. The hydrogen generated from corrosion is allowed to build up, and usually no provision is made to control its concentration. Thus, the hydrogen content of testing waters may vary widely, depending upon the amount of corrosion taking place and the length of exposure time.

The mechanism by which hydrogen enters the Zircaloy is still unknown. Based on this work and that of a previous study[3], it appears that the hydrogen is absorbed as follows: (1) the hydrogen ions produced during corrosion migrate to the cathodic intermetallic compounds in the oxide on the Zircaloy, (2) the hydrogen is discharged on iron-chromium-rich compounds and escapes into the water, or is absorbed in nickel-rich compounds, and (3) the latter then serve as diffusion paths for the hydrogen to migrate throughout the metal. It has been demonstrated that cathodic polarization during

corrosion in high-temperature water results in a marked increase in hydrogen concentration in zirconium-0.5 w/o nickel alloys.[7] It also is known that at least one of the zirconium-nickel compounds will hydride to a greater extent than zirconium.[8]

The uniform distribution of hydrogen throughout the corrosion-tested Zircaloy specimens can be explained on the following basis. The terminal solubility of hydrogen in Zircaloy at the corrosion temperatures of 300 to 400 C is probably about the same as that reported for alpha zirconium, or about 200 to 300 ppm.[9] The amount of hydrogen from the corrosion reaction which entered the Zircaloy at any given time was small. The diffusion rate of hydrogen was sufficiently rapid to avoid exceeding the solubility limit at the metal surface. (This accounts for the absence of a hydride layer at the metal-oxide interface.) Because of the long exposure periods and the fact that the solubility limits were not exceeded, the hydrogen diffused uniformly throughout the specimen. Upon cooling to room temperature, the solubility limit was exceeded and hydride needles precipitated uniformly throughout the specimen. It is possible that the nickel compounds in the Zircaloy could influence these phenomena. The hydrogen distribution would be hastened if hydrogen had a high solubility and a rapid diffusion rate in these compounds.

To better understand the mechanism of hydrogen absorption in Zircaloy-2, it would be necessary to (1) identify the intermetallic compound particles, (2) determine their susceptibility to hydriding from molecular, cathodically produced, and corrosion-reaction hydrogen, and (3) determine the diffusion rate in the compounds of hydrogen absorbed from these sources.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to the Battelle staff members who contributed to this study, including Messrs. J. S. Di Pesa and B. E. White, who melted and fabricated the alloys, Mr. M. A. Van Camp, who performed the hydrogen assays, and Mr. W. N. Stiegelmeyer, who conducted the metallographic examinations.

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APPENDIX

CORROSION-TEST DATA

TABLE A-1. CORROSION-RATE CONSTANTS FOR ZIRCALOY EXPOSED TO 600 F DEGASSED WATER

Alloy Base	Addition, w/o	Transition Time, days	Corrosion-Rate Constants[a] Pretransition k, mg per dm^2	Pretransition n, dimensionless	Posttransition k, mg per dm^2	Posttransition n, dimensionless
Zircaloy-2 (1.60 w/o Sn)	<0.001 Sb	No transition	4.4	0.38	--	--
	0.05 Sb	No transition	6.4	0.30	--	--
	0.20 Sb	No transition	9.5	0.24	--	--
	0.41 Sb	No transition	6.8	0.29	--	--
Modified Zircaloy-2 (1.05 w/o Sn)	<0.001 Sb	No transition	11.2	0.24	--	--
	0.05 Sb	No transition	12.8	0.24	--	--
	0.14 Sb	No transition	17.5	0.19	--	--
	0.46 Sb	No transition	8.0	0.29	--	--
Modified Zircaloy-2 (0.31 w/o Sn)	<0.001 Sb	No transition	10.5	0.33	--	--
	0.06 Sb	No transition	9.5	0.28	--	--
	0.17 Sb	No transition	27.0	0.16	--	--
	0.51 Sb	No transition	6.0	0.33	--	--
Zircaloy-2 (1.60 w/o Sn)	0.03 As	No transition	12.0	0.21	--	--
	0.14 Bi	No transition	19.5	0.17	--	--
	0.11 Te	No transition	15.0	0.22	--	--

(a) For the equation $w = kt^n$ where: w = total weight gain in mg per dm^2, k = extrapolated 1-day intercept of a log-log plot of weight gain versus time, n = slope of the log-log plot, and t = time in days.

TABLE A-2. CORROSION-RATE CONSTANTS FOR ZIRCALOY EXPOSED TO 680 F DEGASSED WATER

Alloy Base	Addition, w/o	Transition Time, days	Corrosion-Rate Constants[a] Pretransition k, mg per dm^2	Pretransition n, dimensionless	Posttransition k, mg per dm^2	Posttransition n, dimensionless
Zircaloy-2 (1.60 w/o Sn)	<0.001 Sb	125	14.0	0.20	0.85	0.83
	0.05 Sb	125	6.60	0.44	2.9	0.63
	0.20 Sb	110	20.0	0.16	0.90	0.84
	0.41 Sb	110	12.0	0.27	0.44	0.97
Modified Zircaloy-2 (1.05 w/o Sn)	<0.001 Sb	85	11.2	0.28	2.0	0.67
	0.05 Sb	130	31.0	0.12	1.7	0.71
	0.14 Sb	110	42.0	0.09	6.0	0.51
	0.46 Sb	110	17.0	0.21	1.8	0.69
Modified Zircaloy-2 (0.31 w/o Sn)	<0.001 Sb	95	11.0	0.32	3.4	0.58
	0.06 Sb	115	9.0	0.31	1.2	0.73
	0.17 Sb	120	15.0	0.23	4.2	0.51
	0.51 Sb	120	14.5	0.21	0.7	0.83
Zircaloy-2 (1.60 w/o Sn)	0.03 As	115	14.0	0.27	0.78	0.88
	0.14 Bi	105	35.0	0.08	2.3	0.67
	0.11 Te	125	35.0	0.10	2.0	0.70

(a) For the equation $w = kt^n$ where: w = total weight gain in mg per dm^2, k = extrapolated 1-day intercept of a log-log plot of weight gain versus time, n = slope of the log-log plot, and t = time in days.

TABLE A-3. CORROSION-RATE CONSTANTS FOR ZIRCALOY EXPOSED TO 750 F 1500-PSI DEGASSED STEAM

Alloy Base	Addition, w/o	Transition Time, days	Corrosion-Rate Constants[a] Pretransition k, mg per dm^2	Pretransition n, dimensionless	Posttransition k, mg per dm^2	Posttransition n, dimensionless
Zircaloy-2 (1.60 w/o Sn)	<0.001 Sb	110	10.8	0.32	0.30	1.09
	0.05 Sb	85	13.0	0.33	1.30	0.84
	0.20 Sb	95	11.6	0.36	0.40	1.10
	0.41 Sb	120	10.0	0.47	0.50	1.20
Modified Zircaloy-2 (1.05 w/o Sn)	<0.001 Sb	65	14.0	0.25	3.4	0.60
	0.05 Sb	75	11.0	0.32	2.2	0.69
	0.14 Sb	90	12.5	0.30	1.7	0.75
	0.46 Sb	85	11.5	0.34	0.45	1.08
Modified Zircaloy-2 (0.31 w/o Sn)	<0.001 Sb	100	12.0	0.28	1.8	0.70
	0.06 Sb	70	11.0	0.29	3.2	0.58
	0.17 Sb	100	14.0	0.25	3.2	0.58
	0.51 Sb	65	11.0	0.33	0.9	0.93
Zircaloy-2 (1.60 w/o Sn)	0.03 As	85	11.5	0.37	0.4	1.13
	0.14 Bi	80	11.0	0.36	1.7	0.80
	0.11 Te	95	12.0	0.35	1.1	0.88

(a) For the equation $w = kt^n$ where: w = total weight gain in mg per dm^2, k = extrapolated 1-day intercept of a log-log plot of weight gain versus time, n = slope of the log-log plot, and t = time in days.

TABLE A-4. CORROSION-RATE CONSTANTS FOR ZIRCALOY EXPOSED TO 680 F WATER WITH 2 ATM OF HYDROGEN

Alloy Base	Addition, w/o	Transition Time, days	Corrosion-Rate Constants[a] Pretransition k, mg per dm^2	Pretransition n, dimensionless	Posttransition k, mg per dm^2	Posttransition n, dimensionless
Zircaloy-2 (1.60 w/o Sn)	<0.001 Sb	110	14.0	0.13	0.01	1.63
	0.05 Sb	110	9.0	0.24	0.03	1.46
	0.20 Sb	105	10.2	0.25	0.05	1.39
	0.41 Sb	95	11.2	0.22	0.02	1.63
Modified Zircaloy-2 (1.05 w/o Sn)	<0.001 Sb	135	9.0	0.24	0.007	1.74
	0.05 Sb	125	9.8	0.22	0.02	1.51
	0.14 Sb	110	10.0	0.25	0.08	1.27
	0.46 Sb	105	9.0	0.25	0.10	1.23
Modified Zircaloy-2 (0.31 w/o Sn)	<0.001 Sb	120	9.0	0.24	0.01	1.68
	0.06 Sb	120	8.5	0.26	0.015	1.59
	0.17 Sb	115	9.5	0.23	0.01	1.68
	0.51 Sb	120	7.3	0.31	0.008	1.72
Zircaloy-2 (1.60 w/o Sn)	0.03 As	95	10.5	0.24	0.05	1.39
	0.14 Bi	100	10.5	0.21	0.07	1.30
	0.11 Te	100	9.5	0.57	0.015	1.66

(a) For the equation $w = kt^n$ where: w = total weight gain in mg per dm^2, k = extrapolated 1-day intercept of a log-log plot of weight gain versus time, n = slope of the log-log plot, and t = time in days.

TABLE A-5. SUMMARY OF CORROSION AND HYDROGEN-ABSORPTION DATA FOR ZIRCALOY EXPOSED TO 600 F DEGASSED WATER

Alloy Base	Addition, w/o	Pretransition			Approximate Transition			Posttransition		
		Exposure Time, days	Total Weight Gain, mg per dm^2	Hydrogen Absorbed, mg per dm^2	Exposure Time, days	Total Weight Gain, mg per dm^2	Hydrogen Absorbed, mg per dm^2	Exposure Time, days	Total Weight Gain, mg per dm^2	Hydrogen Absorbed, mg per dm^2
Zircaloy-2 (1.60 w/o Sn)	<0.001 Sb	56	24.7	1.48	224	34.2	2.05	--	--	--
	0.05 Sb	84	25.2	2.18	224	33.8	3.18	--	--	--
	0.20 Sb	28	23.2	1.75	224	39.3	3.24	--	--	--
	0.41 Sb	56	23.9	1.04	224	34.2	2.04	--	--	--
Modified Zircaloy-2 (1.05 w/o Sn)	<0.001 Sb	28	23.6	1.58	168	40.2	2.50	--	--	--
	0.05 Sb	28	25.0	1.31	84	38.8	2.35	224	44.3	2.81
	0.14 Sb	28	24.5	2.13	56	39.6	3.00	224	50.8	3.80
	0.46 Sb	28	23.7	0.78	224	36.7	1.13	--	--	--
Modified Zircaloy-2 (0.31 w/o Sn)	<0.001 Sb	28	25.5	0.68	56	44.1	1.31	112	60.0	1.73
	0.06 Sb	28	27.0	0.28	168	40.7	0.79	224	49.4	1.31
	0.17 Sb	--	--	--	28	43.0	0.83	112	60.6	1.14
	0.51 Sb	56	24.8	0.75	224	34.2	0.97	--	--	--
Zircaloy-2 (1.60 w/o Sn)	0.03 As	28	26.1	0.75	168	41.6	1.91	--	--	--
	0.14 Bi	28	28.6	1.48	56	40.4	2.17	224	47.5	2.09
	0.11 Te	28	27.4	2.09	56	41.5	3.19	224	51.8	3.84

TABLE A-6. SUMMARY OF CORROSION AND HYDROGEN-ABSORPTION DATA FOR ZIRCALOY EXPOSED TO 680 F DEGASSED WATER

Alloy Base	Addition, w/o	Pretransition			Approximate Transition			Posttransition		
		Exposure Time, days	Total Weight Gain, mg per dm^2	Hydrogen Absorbed, mg per dm^2	Exposure Time, days	Total Weight Gain, mg per dm^2	Hydrogen Absorbed, mg per dm^2	Exposure Time, days	Total Weight Gain, mg per dm^2	Hydrogen Absorbed, mg per dm^2
Zircaloy-2 (1.60 w/o Sn)	<0.001 Sb	14	24.2	1.02	112	39.7	2.04	196	57.2	3.25
	0.05 Sb	14	25.0	1.57	56	39.8	2.62	140	61.7	4.03
	0.20 Sb	7	28.3	2.78	56	41.5	3.31	140	57.0	4.50
	0.41 Sb	14	24.9	1.35	84	39.8	1.48	140	57.9	1.89
Modified Zircaloy-2 (1.5 w/o Sn)	<0.001 Sb	14	24.5	2.12	84	40.6	2.92	168	64.8	4.51
	0.05 Sb	--	--	--	7	39.0	2.36	112	58.9	5.09
	0.14 Sb	--	--	--	7	40.8	4.33	112	62.0	5.47
	0.46 Sb	7	25.3	1.08	56	40.0	1.47	140	68.3	1.98
Modified Zircaloy-2 (0.31 w/o Sn)	<0.001 Sb	14	24.9	1.18	84	41.7	1.74	140	58.8	2.47
	0.06 Sb	28	24.9	0.57	84	38.7	1.23	196	60.1	2.68
	0.17 Sb	7	25.6	1.05	56	40.1	1.63	168	59.9	2.30
	0.51 Sb	14	23.7	1.04	84	41.7	1.46	196	59.3	2.49
Zircaloy-2 (1.60 w/o Sn)	0.03 As	7	24.4	0.80	56	42.7	2.32	140	55.7	3.30
	0.14 Bi	--	--	--	7	41.2	3.06	140	65.4	2.12
	0.11 Te	--	--	--	7	40.3	2.13	112	59.9	6.29

TABLE A-7. SUMMARY OF CORROSION AND HYDROGEN-ABSORPTION DATA FOR ZIRCALOY EXPOSED TO 750 F 1500-PSI DEGASSED STEAM

Alloy Base	Addition, w/o	Pretransition			Approximate Transition			Posttransition		
		Exposure Time, days	Total Weight Gain, mg per dm^2	Hydrogen Absorbed, mg per dm^2	Exposure Time, days	Total Weight Gain, mg per dm^2	Hydrogen Absorbed, mg per dm^2	Exposure Time, days	Total Weight Gain, mg per dm^2	Hydrogen Absorbed, mg per dm^2
Zircaloy-2 (1.60 w/o Sn)	<0.001 Sb	14	26.0	1.55	42	38.8	1.74	140	69.9	2.61
	0.05 Sb	7	26.2	1.54	28	40.3	2.27	112	71.6	3.69
	0.20 Sb	7	24.7	1.30	28	37.7	2.34	112	72.7	3.82
	0.41 Sb	7	25.9	1.07	28	41.2	1.87	--	--	--
Modified Zircaloy-2 (1.05 w/o Sn)	<0.001 Sb	7	25.7	1.93	42	39.4	3.09	168	70.1	4.34
	0.05 Sb	28	27.3	2.74	42	40.2	3.13	140	71.8	4.38
	0.14 Sb	7	24.6	2.17	42	42.0	3.64	196	86.8	5.81
	0.46 Sb	7	24.4	1.54	42	40.7	2.84	112	71.8	4.14
Modified Zircaloy-2 (0.31 w/o Sn)	<0.001 Sb	7	24.8	1.43	42	39.7	1.76	196	70.4	3.31
	0.06 Sb	28	28.3	1.17	42	40.3	1.58	168	67.4	2.46
	0.17 Sb	7	24.0	1.38	28	39.4	2.01	168	66.8	3.01
	0.51 Sb	7	25.0	1.48	42	40.8	2.14	112	69.5	2.36
Zircaloy-2 (1.60 w/o Sn)	0.03 As	7	25.1	0.95	28	39.1	1.64	112	79.3	3.68
	0.14 Bi	7	25.1	1.30	28	43.0	2.14	112	72.8	3.58
	0.11 Te	7	25.6	1.90	28	40.5	2.56	112	73.0	4.77

TABLE A-8. SUMMARY OF CORROSION AND HYDROGEN-ABSORPTION DATA FOR ZIRCALOY EXPOSED TO 600 F WATER WITH 2 ATM OF HYDROGEN

Alloy Base	Addition, w/o	Pretransition			Approximate Transition			Posttransition		
		Exposure Time, days	Total Weight Gain, mg per dm^2	Hydrogen Absorbed, mg per dm^2	Exposure Time, days	Total Weight Gain, mg per dm^2	Hydrogen Absorbed, mg per dm^2	Exposure Time, days	Total Weight Gain, mg per dm^2	Hydrogen Absorbed, mg per dm^2
Zircaloy-2 (1.60 w/o Sn)	<0.001 Sb	224	33.3	1.32	224	40.2	2.09	--	--	--
	0.05 Sb	14	25.2	1.81	224	44.2	3.44	--	--	--
	0.20 Sb	--	--	--	224	39.9	3.12	224	53.3	3.63
	0.41 Sb	--	--	--	224	47.8	2.59	224	51.2	2.69
Modified Zircaloy-2 (1.05 w/o Sn)	<0.001 Sb	14	26.5	2.37	224	49.8	3.88	224	59.4	3.88
	0.05 Sb	14	26.3	1.61	224	41.0	2.56	224	55.0	2.56
	0.14 Sb	14	23.3	2.46	--	--	--	224	53.6	3.52
	0.46 Sb	14	24.9	1.11	224	39.8	2.72	--	--	--
Modified Zircaloy-2 (0.31 w/o Sn)	<0.001 Sb	--	--	--	14	41.5	1.36	224	65.5	2.10
	0.06 Sb	14	26.4	0.33	--	--	--	224	60.2	1.37
	0.17 Sb	--	--	--	224	35.2	0.82	224	71.4	2.39
	0.51 Sb	--	--	--	224	40.3	1.52	--	--	--
Zircaloy-2 (1.60 w/o Sn)	0.03 As	14	26.5	0.89	224	41.9	1.19	--	--	--
	0.14 Bi	--	--	--	14	38.4	2.33	224	55.2	1.99
	0.11 Te	--	--	--	14	39.5	3.12	224	63.1	4.43

TABLE A-9. SUMMARY OF CORROSION AND HYDROGEN-ABSORPTION DATA FOR ZIRCALOY EXPOSED TO 680 F WATER WITH 2 ATM OF HYDROGEN

Alloy Base	Addition, w/o	Pretransition			Approximate Transition			Posttransition		
		Exposure Time, days	Total Weight Gain, mg per dm^2	Hydrogen Absorbed, mg per dm^2	Exposure Time, days	Total Weight Gain, mg per dm^2	Hydrogen Absorbed, mg per dm^2	Exposure Time, days	Total Weight Gain, mg per dm^2	Hydrogen Absorbed, mg per dm^2
Zircaloy-2 (1.60 w/o Sn)	<0.001 Sb	56	25.1	1.02	--	--	--	168	60.3	2.17
	0.05 Sb	56	24.4	1.18	--	--	--	168	52.3	2.32
	0.20 Sb	56	24.7	1.44	140	50.4	2.08	140	56.0	2.08
	0.41 Sb	56	25.6	1.24	140	42.9	1.44	140	57.0	1.73
Modified Zircaloy-2 (1.05 w/o Sn)	<0.001 Sb	56	25.1	1.71	168	37.4	2.26	168	58.4	2.71
	0.05 Sb	56	25.1	1.90	168	46.6	2.52	168	57.8	2.85
	0.14 Sb	56	26.1	2.05	140	38.9	2.61	168	59.7	2.98
	0.46 Sb	56	24.9	1.26	140	45.7	1.87	168	55.6	1.87
Modified Zircaloy-2 (0.31 w/o Sn)	<0.001 Sb	56	24.4	0.97	168	34.2	1.15	168	62.6	1.38
	0.06 Sb	56	25.1	0.91	168	37.9	1.27	168	66.7	1.76
	0.17 Sb	56	25.0	1.13	168	36.2	1.76	168	68.4	1.83
	0.51 Sb	56	25.0	0.93	--	--	--	168	68.0	1.86
Zircaloy-2 (1.60 w/o Sn)	0.03 As	56	25.5	1.40	140	50.3	1.86	168	58.3	2.03
	0.14 Bi	56	24.6	0.80	140	45.0	1.14	168	69.6	1.70
	0.11 Te	56	24.9	1.71	140	40.1	2.40	168	68.1	3.50

TABLE A-10. SUMMARY OF CORROSION AND HYDROGEN-ABSORPTION DATA FOR ZIRCALOY EXPOSED TO 750 F 1500-PSI STEAM WITH 2 ATM OF HYDROGEN

Alloy Base	Addition, w/o	Pretransition			Approximate Transition			Posttransition		
		Exposure Time, days	Total Weight Gain, mg per dm^2	Hydrogen Absorbed, mg per dm^2	Exposure Time, days	Total Weight Gain, mg per dm^2	Hydrogen Absorbed, mg per dm^2	Exposure Time, days	Total Weight Gain, mg per dm^2	Hydrogen Absorbed, mg per dm^2
Zircaloy-2 (1.60 w/o Sn)	<0.001 Sb	7	25.3	0.85	--	--	--	224	41.5	4.86
	0.05 Sb	7	26.7	1.54	--	--	--	224	158.0	5.92
	0.20 Sb	7	25.7	1.19	--	--	--	224	166.0	5.75
	0.41 Sb	--	--	--	7	41.1	1.56	224	278.0	5.01
Modified Zircaloy-2 (1.05 w/o Sn)	<0.001 Sb	7	27.3	2.03	--	--	--	224	98.0	5.34
	0.05 Sb	7	26.3	2.32	--	--	--	224	110.0	5.87
	0.14 Sb	7	26.1	2.81	14	39.7	2.71	224	122.0	6.66
	0.46 Sb	--	--	--	--	--	--	224	161.0	4.67
Modified Zircaloy-2 (0.31 w/o Sn)	<0.001 Sb	7	24.9	1.58	--	--	--	224	83.2	3.85
	0.06 Sb	14	24.8	1.85	--	--	--	224	85.9	3.66
	0.17 Sb	7	25.8	1.73	--	--	--	224	92.2	4.60
	0.51 Sb	7	26.1	1.74	--	--	--	224	144.0	4.67
Zircaloy-2 (1.60 w/o Sn)	0.03 As	7	28.0	1.32	--	--	--	224	156.0	6.88
	0.14 Bi	--	--	--	--	--	--	--	--	--
	0.11 Te	7	25.9	1.73	--	--	--	224	147.0	7.09