ARMOUR RESEARCH FOUNDATION
of
ILLINOIS INSTITUTE OF TECHNOLOGY
Technology Center
Chicago 16, Illinois

DELAYED FAILURE HYDROGEN EMBRITTLEMENT OF ZIRCONIUM

ARF 2230-3
(Quarterly Report No. 1)
September 15, 1961 to December 14, 1961

Contract No. AT(11-1)-578
Project Agreement No. 14

U.S. Atomic Energy Commission
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois

Attention: Mr. Fred C. Mattmueller
Director
Contracts Division

January 3, 1962

DELAYED FAILURE HYDROGEN EMBRITTLEMENT OF ZIRCONIUM

ABSTRACT

The purpose of this investigation is to determine the extent to which zirconium exhibits delayed failure (static fatigue) as caused by a combination of absorbed hydrogen and applied stress. Both notched and unnotched specimens of unalloyed zirconium and Zircaloy-2 are being initially hydrogenated to 200 ppm by means of a modified Sieverts apparatus, and delayed failure studies are proceeding at room-temperature. Thus far, only preliminary data on unnotched, unalloyed zirconium are available; at the 200 ppm hydrogen level, this material appears to be relatively insensitive to delayed failure at room-temperature.

241 02

DELAYED FAILURE HYDROGEN EMBRITTLEMENT OF ZIRCONIUM

I. INTRODUCTION

This is the first Quarterly Report, covering the period September 15 to December 14, 1961, on Contract No. AT(11-1)-578, Project Agreement No. 14. This investigation is being conducted under the auspices of the USAEC/AECL Collaborative Program.

It was recognized several years ago that zirconium absorbs hydrogen during corrosion in superheated water and steam. Shortly after this, the loss of impact properties after exposure to high-temperature water or steam was attributed to the presence of zirconium hydride as a grain boundary and/or matrix platelet phase. In recent years, a considerable number of investigations have been pursued for the purpose of increasing knowledge of this phenomenon as well as finding means of eliminating this serious embrittlement problem. In these investigations, the impact test was, very logically, almost exclusively employed as a method of evaluation; such an approach, however, has resulted in an almost complete neglect of perhaps an equally or more important manifestation of hydrogen occlusion--namely, the delayed failure phenomenon. Thus, the purpose of the present investigation is to determine the extent to which zirconium exhibits delayed failure (static fatigue) as caused by a combination of absorbed hydrogen and applied stress.

That the long-time mechanical properties of zirconium are important design considerations cannot be disputed when one considers that certain in-core reactor components, such as pressure tubes and structural elements, should have a service lifetime of up to 20 years. Impact tests are not able to predict long-time mechanical behavior. Moreover, current theories for hydrogen embrittlement do not preclude the possibility of static fatigue occurring in zirconium. While this phenomenon is usually associated with high-strength steels and other body-centered cubic metals, delayed failure has been observed for titanium alloys and even face-centered cubic alloys. One does not know, a priori, that zirconium does not exhibit delayed failure. In fact, considering the amount of corrosion hydrogen pickup during reactor service and the possibility of subsequent localized concentration due to migration in thermal and mechanical stress gradients--as well as the utilization of higher strength alloys--one might anticipate some susceptibility to delayed failure.

II. MATERIALS, APPARATUS, AND PROCEDURES

Delayed failure studies are being carried out initially on notched and unnotched specimens of unalloyed zirconium and Zircaloy-2; the static fatigue specimens contain approximately 200 ppm hydrogen, introduced by means of a modified Sieverts apparatus, and initial evaluation of delayed failure susceptibility is carried out at room-temperature.

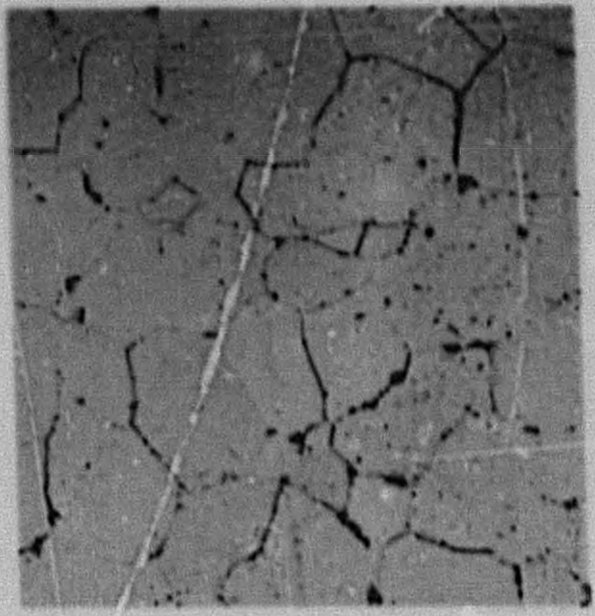
The above materials are in the form of 1/16 x 1 inch fully annealed strip; the ingot analysis of these materials is presented in Table I. For the wrought, fully annealed materials, the hardness and grain size of unalloyed zirconium are 175 VHN and 324 grain/mm^2; for Zircaloy-2, 197 VHN and 1650 grains/mm^2. The microstructures of these materials are shown in Figures 1 and 2. Both notched and unnotched specimens are machined from as-received strip to dimensions shown in Figure 3 and Figure 4, respectively. The notch radius of 0.004 inch is rather easily obtained by conventional grinding; however, this dimension is further reduced to about 0.001 inch by slightly depressing a 44° knife edge into the base of the notch. (Subsequent annealing causes recrystallization at this region without excessive grain coarsening.) All notched specimens, therefore, have a 0.001 inch radius at the base; utilizing the specimen widths and the above radius, a theoretical stress-concentration K_t of 10 is calculated. Specimens are pickled in a solution of $45HNO_3$-$5HF$-$50H_2O$, rinsed in ethyl alcohol, and then placed in the Sieverts apparatus for hydrogen charging. (For notched specimens, pickling is carried out prior to reduction of the notch radius. After specimen cleaning, lint-free gloves are required in handling so as to prevent surface contamination which might adversely affect the Sieverts hydriding operation.)

Figure 5 is a schematic representation of a modified Sieverts apparatus; without entering into a detailed description of this unit,

TABLE I

SUPPLIER'S ANALYSIS OF ZIRCONIUM AND ZIRCALOY-2 INGOTS

Element	Content, ppm	
	Zirconium	Zircaloy-2
Sn	< 10	1.52 w/o
Fe	395	0.10 w/o
Cr	87	0.09 w/o
Ni	10	0.06 w/o
C	60	135
N	18	25
O	798	- -
H	3.5	13
Al	< 25	38
B	< 0.2	< 0.2
Cd	< 0.3	< 0.3
Co	< 5	< 5
Cu	< 25	< 20
Hf	- -	57
Mg	< 10	< 10
Mn	< 10	15
Mo	< 10	< 10
Pb	< 5	15
Si	69	45
Ti	< 20	< 20
U	- -	1.3
V	< 5	< 20
W	< 25	< 40
Zn	< 50	- -



Neg. No. 22355 **Mag. X250**

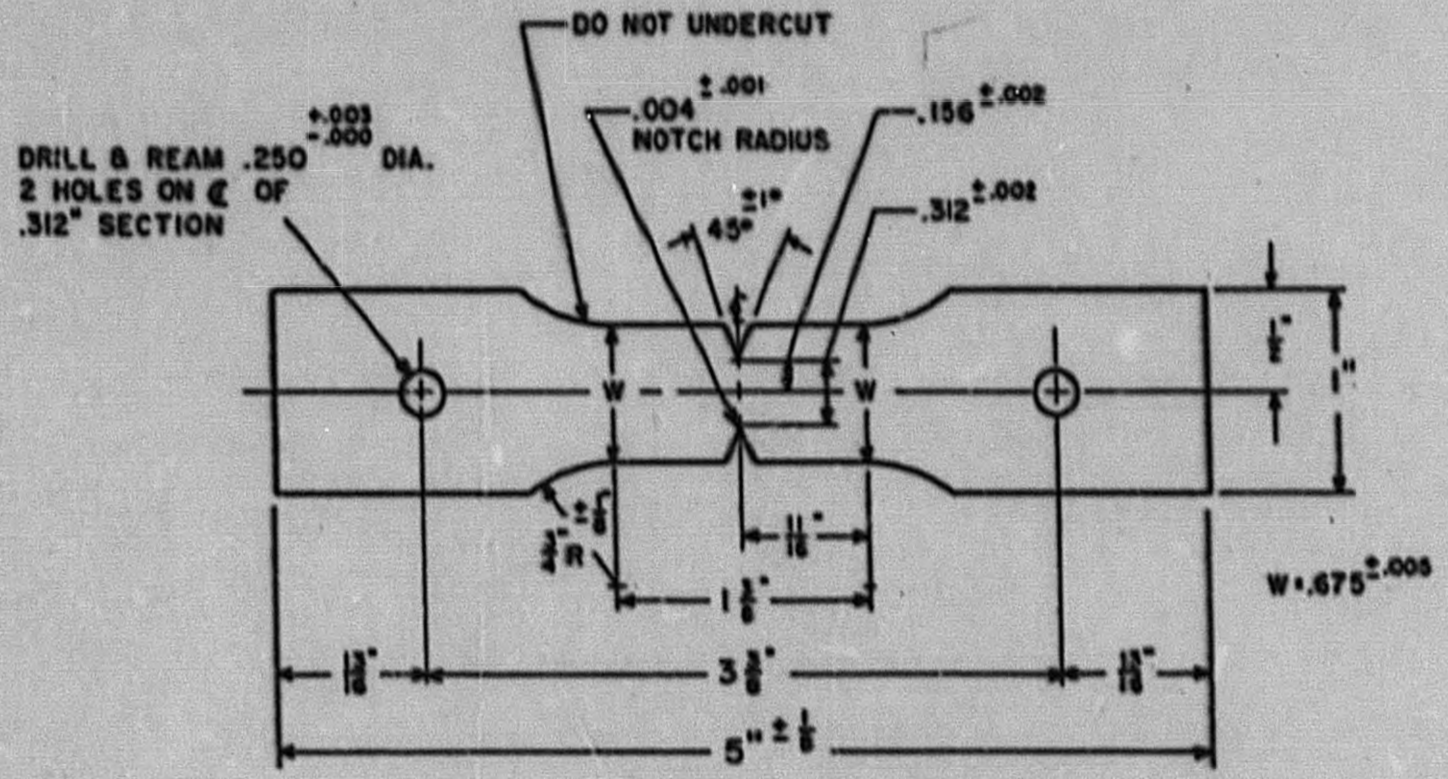
Fig. 1

Microstructure of unalloyed zirconium vacuum annealed at 800°C for 1 hour, slowly cooled. Hydrogen content is approximately 15 ppm.
Etchant: 1HF-1HNO$_3$-3 glycerin

Neg. No. 22354 **Mag. X250**

Fig. 2

Microstructure of Zircaloy-2 vacuum annealed at 800°C for 1 hour, slowly cooled. Hydrogen content is approximately 10 ppm.
Etchant: 1HF-1HNO$_3$-3 glycerin



MAKE SYMMETRICAL ABOUT ℄

SCALE: FULL SIZE

TOLERANCES: ± 1/64" EXCEPT AS NOTED

FIG. 3 - NOTCHED TENSILE AND DELAYED FAILURE SPECIMEN.

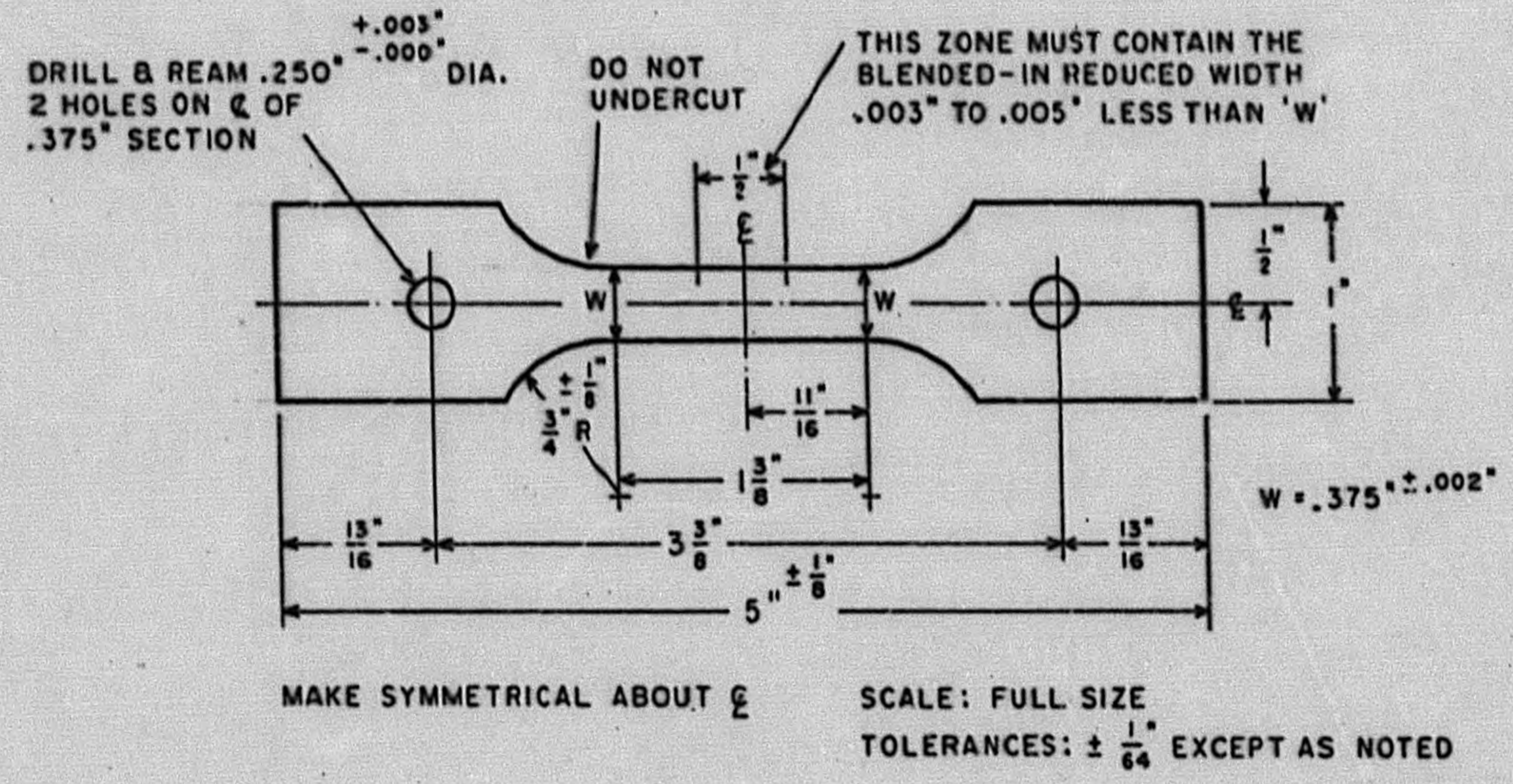


FIG. 4 - UNNOTCHED TENSILE AND DELAYED FAILURE SPECIMEN.

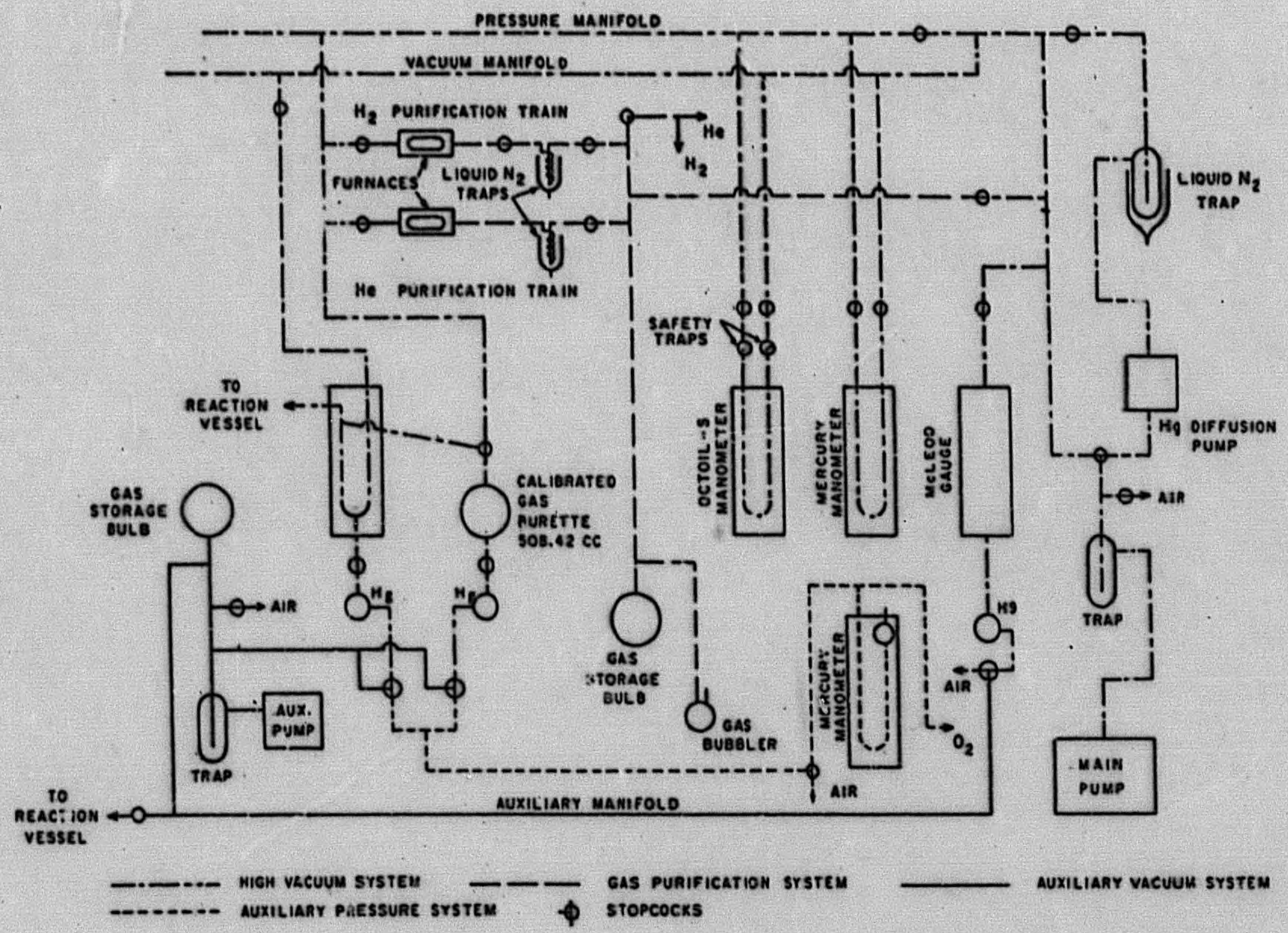


FIG. 5 - SCHEMATIC DIAGRAM OF SIEVERTS APPARATUS

it essentially allows--by means of various manometers, vacuum lines, and a calibrated gas burette--for measuring out, isolating, and introducing a quantity of hydrogen to give the desired composition in a specimen of a given weight. Thus far, all specimens have been charged with 200 ppm hydrogen; at this level, past experience has shown that an accuracy of about 10 per cent is obtained. At higher hydrogen contents, the accuracy greatly improves. In hydrogen charging, the specimen is first vacuum (approximately 0.02 micron) annealed for one hour at 800°C within the reaction vessel; maintaining this temperature, the predetermined amount of hydrogen is introduced to the specimen, and the reaction is completed within two minutes. The specimen is held at 800°C for 30 minutes and then slowly cooled. Static fatigue evaluation is carried on lever-arm creep/stress-rupture stands, and dynamic tensile tests are performed on a 10,000 pound capacity Instron tensile machine.

III. RESULTS AND DISCUSSION

To check the content and distribution of hydrogen in delayed failure specimens, Sieverts hydriding experiments were performed on two 5-inch strips of unalloyed zirconium; 200 ppm was the intended hydrogen content, and the temperature was constant at 800°C ± 2°C over the specimen length. The results of vacuum fusion analysis on specimens from end to center to end were as follows (in ppm):

209	205
218	203
205	185

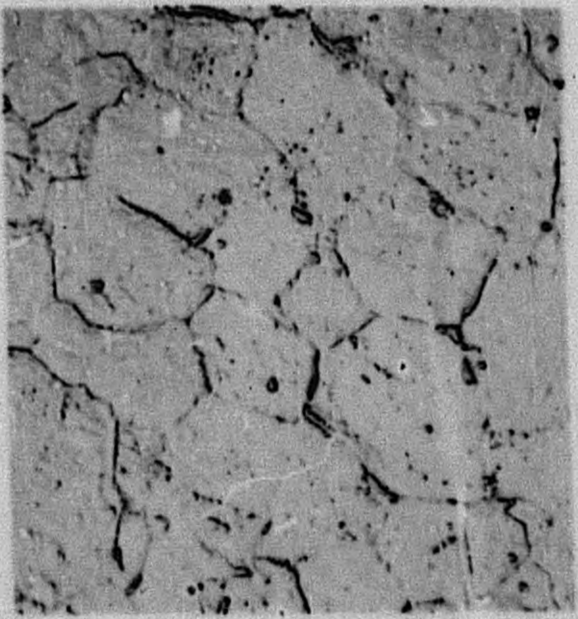
Both the hydrogen level and distribution appear satisfactory and within the accuracy of the experimental method. Moreover, considering the inherent scatter of data in vacuum-fusion analysis, the techniques employed for hydrogenating appear satisfactory.

Figures 6 and 7 are photomicrographs of hydrided zirconium and Zircaloy-2 containing about 200 ppm hydrogen. The hydride phase is predominantly concentrated in the grain boundaries; however, some small hydride aciculae are observed within the grains--probably formed by precipitation along a specific crystallographic plane.

Neg. No. 22352 **Mag. X500**

Fig. 6

Microstructure of unalloyed zirconium containing about 200 ppm hydrogen. The zirconium hydride phase is heavily concentrated in the grain boundaries.
Etchant: 1HF-1HNO$_3$-3 glycerin.



Neg. No. 22353 **Mag. X500**

Fig. 7

Microstructure of Zircaloy-2 containing about 200 ppm hydrogen. The zirconium hydride precipitate is concentrated in the grain boundaries.
Etchant: 1HF-1HNO$_3$-3 glycerin.

To render delayed failure investigations more meaningful and to allow judicious use of hydrogenated specimens, dynamic tensile tests (0.05 inch/minute crosshead speed) were carried out on unalloyed zirconium and Zircaloy-2. Specimens were both notched and unnotched as well as in the as-received and hydrogenated condition; the results of these tests are summarized in Table II. Comparing the ultimate tensile strength of the two materials, it is rather surprising to note a higher value for unalloyed zirconium. Perhaps the Zircaloy-2 has a very low oxygen content as compared to the 800 ppm in unalloyed zirconium; vacuum fusion analysis for oxygen is presently being carried out. For unnotched specimens, there is only a slight change in tensile strength with addition of 200 ppm hydrogen; the total elongation, however, is significantly decreased, as would be expected from the microstructural appearance. Notice that the introduction of a notch in as-received material results in an increased ultimate tensile strength; this behavior is due to constraint of the surrounding material from yielding and indicates that the alloy is not notch sensitive at a loading rate of 0.05 inch/minute. When hydrogen is introduced to this specimen, however, the tensile strength then slightly decreases which indicates a small tendency toward notch sensitivity.

The delayed failure investigation has been initiated at room-temperature on notched and unnotched specimens of unalloyed zirconium containing 200 ppm hydrogen; a summary of applied stresses and failure time, thus far, is given in Table III. For unnotched specimens, the failure times were rather short at high stress levels; however, the mode of fracture was by creep. It appears that no further fractures will be observed within the 1000-hour test period; these data suggest that unnotched specimens of unalloyed zirconium at room temperature with a hydrogen content of 200 ppm present as a hydride precipitate are not susceptible to static fatigue. For notched specimens, the time of fracture occurrence at the applied stresses shown in Table III indicates perhaps a slightly greater tendency for delayed failure; however, the short evaluation time does not allow a meaningful conclusion.

TABLE II

DYNAMIC TENSILE PROPERTIES OF UNALLOYED ZIRCONIUM AND ZIRCALOY-2

Condition	Ultimate Tensile Strength, psi	Yield Stress, psi (0. 2% offset)	Total Elongation, %
	Zirconium		
Unnotched, As-Received	51, 000	19, 200	32. 5
Unnotched, 200 ppm H_2	51, 400	21, 200	27. 3
Notched, As-Received	55, 100	28, 700	(6. 7)*
Notched, 200 ppm H_2	51, 900	28, 700	(4. 2)*
	Zircaloy-2		
Unnotched, As-Received	45, 300	32, 000	41. 5
Unnotched, 200 ppm H_2	47, 100	31, 800	34. 5
Notched, As-Received	64, 200	44, 300	(10. 9)*
Notched, 200 ppm H_2	62, 200	41, 800	(6. 2)*

---

* Value taken from load-extension curve; deformation was confined, however, to the area around the base of the notch.

TABLE III

DELAYED FAILURE INVESTIGATION OF UNALLOYED ZIRCONIUM CONTAINING 200 PPM HYDROGEN

Applied Stress, psi	Time to Failure, hr
Unnotched Specimens	
43, 500	6.0
41, 500	49.5
39, 500	129.6
36, 000	-- *
30, 000	--
27, 000	--
25, 000	--
20, 000	--
18, 000	--
Notched Specimens	
47, 900	0.066
44, 200	22.3
40, 400	-- **
37, 200	--
31, 900	--
26, 600	--

* No failure; time of test is about 900 hours.
** No failure; time of test is about 180 hours.

241 14

IV. FUTURE WORK

Evaluation of unalloyed zirconium with 220 ppm hydrogen will continue to the arbitrarily chosen maximum failure time of 1000 hours. Hydrogenating of Zircaloy-2 specimens to the 200 ppm level is proceeding, and static fatigue investigations will be initiated during the next report period. As yet, no word has been received on the availability of Zr-2.5Nb; this higher strength alloy might exhibit a more pronounced tendency for delayed failure. Static fatigue evaluation of zirconium and Zircaloy-2 is being considered at higher hydrogen levels.

V. CONCLUSIONS

An investigation is being pursued for the purpose of determining the degree of susceptibility of zirconium and zirconium alloys to delayed failure as caused by hydrogen occlusion and applied stress. Only preliminary and relatively short-time data are available; it appears, however, that unalloyed zirconium containing approximately 200 ppm hydrogen--and in the absence of stress concentrations--is relatively insensitive to delayed failure at room temperature.

VI. LOGBOOKS AND CONTRIBUTING PERSONNEL

The data presented in this report are recorded in ARF Logbooks Nos. C-11680, C-11681, and C-11682.

Personnel contributing to this work are the following:

L. J. Adamski - Project Technician
F. C. Holtz - Group Leader
D. Weinstein - Project Engineer

Respectfully submitted,

ARMOUR RESEARCH FOUNDATION OF
ILLINOIS INSTITUTE OF TECHNOLOGY

D. Weinstein, Associate Metallurgist

F. C. Holtz, Senior Metallurgist

DW/rh
Tech Rev - CRS