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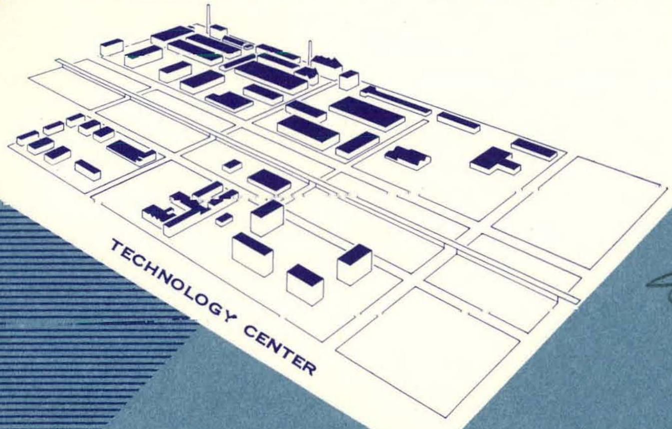
ARF 2230-12
(Summary Report)

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY



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

DELAYED FAILURE HYDROGEN EMBRITTLEMENT OF ZIRCONIUM

U. S. Atomic Energy Commission
Chicago Operations Office
Argonne, Illinois

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

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ARF 2230-12
(Summary Report)
September 15, 1961 - September 14, 1962

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for

U.S. Atomic Energy Commission
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October 10, 1962

DELAYED FAILURE HYDROGEN EMBRITTLEMENT OF ZIRCONIUM

ABSTRACT

The purpose of this investigation is to determine the extent to which zirconium and zirconium alloys exhibit delayed failure (static fatigue) as caused by a combination of absorbed hydrogen and applied stress. Susceptibility to time-dependent fracture was evaluated for unalloyed zirconium and Zircaloy-2 with 200 ppm and 500 ppm hydrogen as well as for an experimental Zr-Al-Sn-Mo alloy and the Canadian Zr-2.5Nb cladding material.

For unalloyed zirconium and Zircaloy-2 containing up to 500 ppm hydrogen, no room-temperature, time-dependent fracture occurred which could be definitely attributed to the delayed failure phenomenon; an increased grain size, 20 per cent cold deformation by rolling, or corrosion in 750° F steam does not significantly affect this behavior. The curve of applied stress versus time to failure at room temperature for the high-strength Zr-Al-Sn-Mo alloy containing 500 ppm hydrogen established a strong susceptibility to delayed failure due to hydrogen absorption; studies on vacuum-annealed material showed no failures. Further, reduced temperatures indicate that the occurrence of static fatigue is temperature dependent. Data for heat-treated Zr-2.5Nb containing 500 ppm hydrogen indicate that this material is moderately sensitive to delayed failure at room temperature; higher hydrogen contents caused a greatly increased susceptibility to time-dependent fracture.

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DELAYED FAILURE HYDROGEN EMBRITTLEMENT OF ZIRCONIUM

I. INTRODUCTION

This report summarizes work performed during the period September 15, 1961, to September 14, 1962 on Contract No. AT(11-1)-578, Project Agreement No. 14. This investigation was conducted under the auspices of the USAEC/AECL Collaborative Program.

The term "delayed failure" (or static fatigue) can be defined as the time-dependent fracture of a material due to a combination of absorbed hydrogen and applied stress. Such behavior is well known in steels,(1, 2) where as little as 2 ppm hydrogen can cause embrittlement, and in certain titanium alloys.(2, 3) For zirconium, it is well established that hydride precipitates markedly decrease the impact strength;(4) however, very little work has been reported on studies concerning static fatigue in this material. Thus, the purpose of this investigation was to determine whether or not zirconium or zirconium alloys exhibit delayed failure due to a combination of absorbed hydrogen and applied stress.

The majority of investigations on hydrogen effects on mechanical properties of zirconium have employed impact tests or dynamic tensile tests. From this voluminous accumulation of data, one cannot submit, a priori, that zirconium does not exhibit delayed failure. In fact, certain experimental evidence exists which suggests that such behavior is possible in zirconium. The Petch theory(5) of hydrogen embrittlement in steel, for example, postulates that hydrogen adsorbed on a dislocation crack nucleus can lower the surface energy which then causes a lowering of fracture stress and concomitant crack propagation. The small quantity of hydrogen in solution with zirconium could, to some extent, contribute to embrittlement in a manner analogous to the case for steel. Further, Westlake(6) has shown that hydride platelets act as effective barriers to slip and twinning dislocations, and the stress generated at the head of the pile-up can cause fracture of the hydride.

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It is possible then for this crack to propagate into the zirconium matrix. If the matrix is ductile, the crack tip will be blunted and very little propagation is observed. However, if the matrix is highly alloyed and the ductility is low, it may be possible for crack propagation to occur and--under a constant applied load--lead to delayed failure. In addition, the occurrence of static fatigue in the structurally similar element titanium suggests that zirconium might exhibit this phenomenon.

Indeed, a report of delayed failure susceptibility of Zircaloy-2 has recently been issued by Ostberg(7) in Sweden. He has obtained a static fatigue curve for hydrogen annealed (550° C, 16 hr) material showing failure characteristics similar to those for titanium and steel. At a stress just below the notched tensile strength, fracture occurred in one minute; at a stress of 70 per cent of the tensile strength, fracture occurred at approximately 1600 hours. The shape of the curve was not asymptotic to any particular lower critical stress, and it appeared that fracture would occur after very long times at stresses somewhat below 70 per cent of the tensile stress. Moreover, resistivity-versus-time curves for stressed, hydrogenated specimens exhibited a step-like increase with time. According to Troiano,(8) the rising parts of the steps are indications of crack propagation, and the horizontal parts correspond to arrest of crack growth. Metallographic inspection confirmed this behavior. (In correspondence with Ostberg, he indicates that only certain lots of Zircaloy-2 exhibited delayed failure; he has not yet been able to correlate this behavior with composition, metallurgical history, or any other parameter. One should also note that the major study area was slow strain-rate embrittlement; experimental evidence was also obtained for this phenomenon in Zircaloy-2--just as in certain titanium alloys.(9))

Considering the large number of anomalous zirconium reactor component failures, one realizes that perhaps delayed failure studies might provide evidence for explanation of failures and lead to more definite design and operating criteria. In certain respects, reactor operation provides at least some of the necessary conditions required for delayed failure--namely, hydrogen absorption, stress, and time. The expected service lifetime of fuel cladding and certain in-core structural components or pressure tubes is of the order of months or years; the time factor is certainly present as well

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as complex states of stress. Zircaloy-2 picks up anywhere from 25 to 50 per cent of the total hydrogen released from the corrosion reaction; over a long operating time, concentrations on the order of 200 ppm may be encountered. This situation is further intensified by the possibility of localized high hydrogen concentrations due to migration in a thermal gradient(10, 11) or directional hydride precipitation perpendicular to a tensile stress.(12) Thus, the conditions for hydrogen absorption are present in the pressurized water reactor environment; from this set of conditions, it seems that investigation of delayed failure susceptibility of zirconium is imperative. Moreover, with zirconium development effort aimed at producing, among other things, higher strength alloys, the possibility of observing static fatigue failure is increased.

II. MATERIALS, APPARATUS, AND EXPERIMENTAL PROCEDURE

The dynamic tensile and delayed failure specimens of unalloyed zirconium and Zircaloy-2, in both the notched and the unnotched condition, were machined from 0.062 inch thick sheet in the fully annealed condition. The alloy Zr-2.5Nb was obtained* as hot-rolled sheet of 0.050 inch thickness, and the Atomics International sodium-cooled reactor cladding material, Zr-1.25Al-1Sn-1Mo, was available as hot-rolled sheet of various thicknesses. The supplier's chemical analysis of each material, with the exception of Zr-Al-Sn-Mo, is presented in Table I; no impurity analysis is available for the Atomics International alloy. (Since a report was made of only certain lots of Zircaloy-2 exhibiting delayed failure susceptibility, sheet material supplied by two other sources was also evaluated; chemical analyses for these materials are not available.)

The specimen dimensions for notched and unnotched specimens of unalloyed zirconium, Zircaloy-2, and Zr-Al-Sn-Mo are presented in Figure 1 and Figure 2, respectively. Reduced size specimens were used for evaluation of Zr-2.5Nb due to the limited supply of material; the dimensions of these specimens, both notched and unnotched, are shown in Figure 3 and Figure 4, respectively.

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* The authors wish to express their thanks to the AECL Chalk River Laboratory for supplying this material.

TABLE I

CHEMICAL ANALYSIS OF THREE SHEET MATERIALS EVALUATED FOR STATIC FATIGUE FAILURE

	Concentration, ppm		
Element	Unalloyed Zr	Zircaloy-2	Zr-2.5Nb
Sn	< 10	1.52%	28
Fe	400	0.10%	1010
Cr	87	0.09%	13
Ni	10	0.05%	20
Nb	--	--	2.67%
C	60	135	150
O	798	977	1160
H	4	13	14
N	18	26	22
Al	< 25	38	28
B	< 0.2	< 0.2	< 0.3
Cd	< 0.3	< 0.3	< 0.3
Co	< 5	< 5	< 10
Cu	< 25	< 20	< 20
Hf	57	--	< 125
Mg	< 10	< 10	< 10
Mn	< 10	15	< 25
Mo	< 10	< 10	< 10
Pb	< 5	15	< 20
Si	69	45	16
Ti	< 20	< 20	< 20
U	--	1.3	< 0.3
V	< 5	< 20	< 10
W	< 25	< 40	152
Zn	< 50	--	--
Ingot Hardness	119 BHN	167 BHN	195 BHN

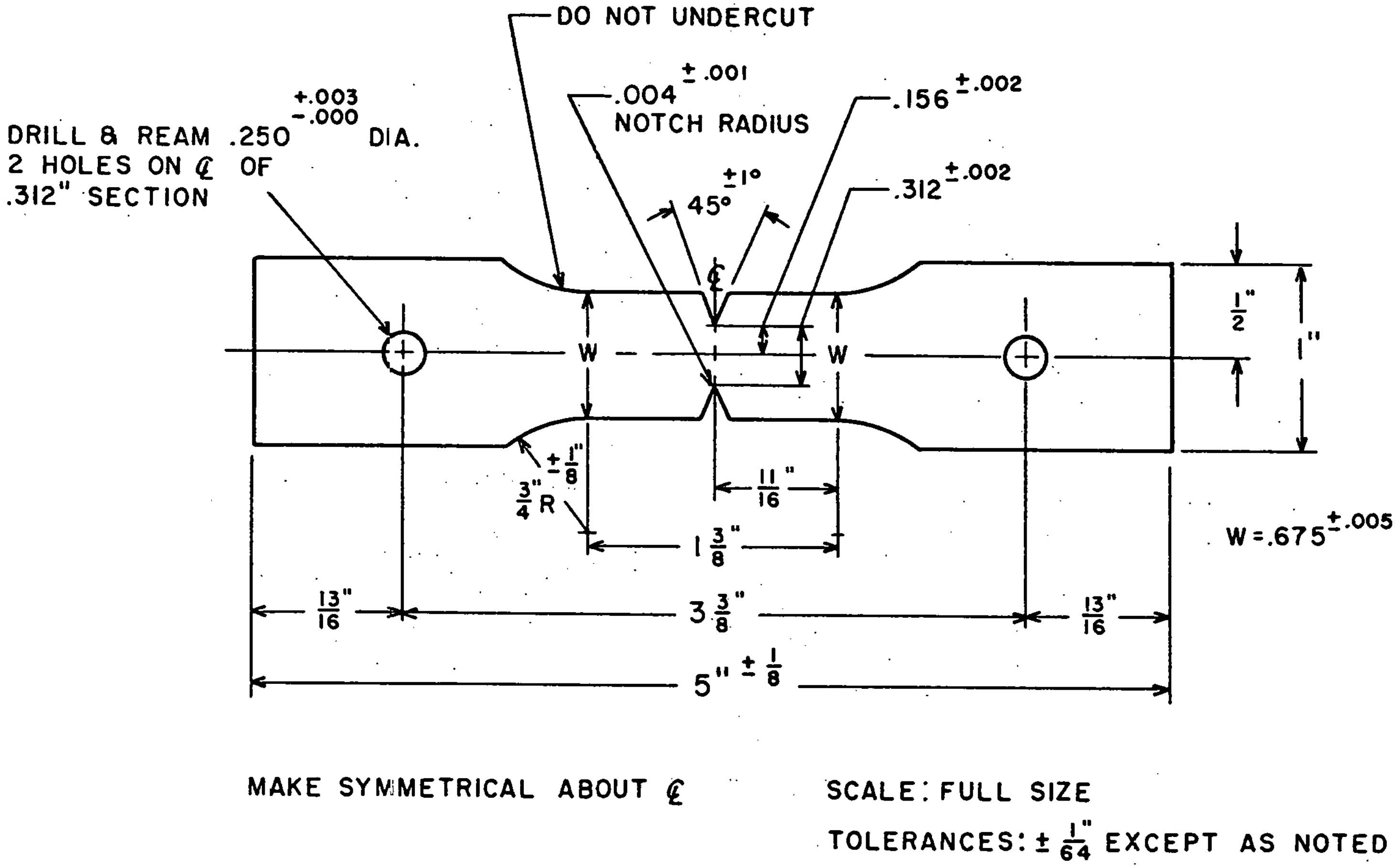

FIG. 1 - NOTCHED TENSILE AND DELAYED FAILURE SPECIMEN.

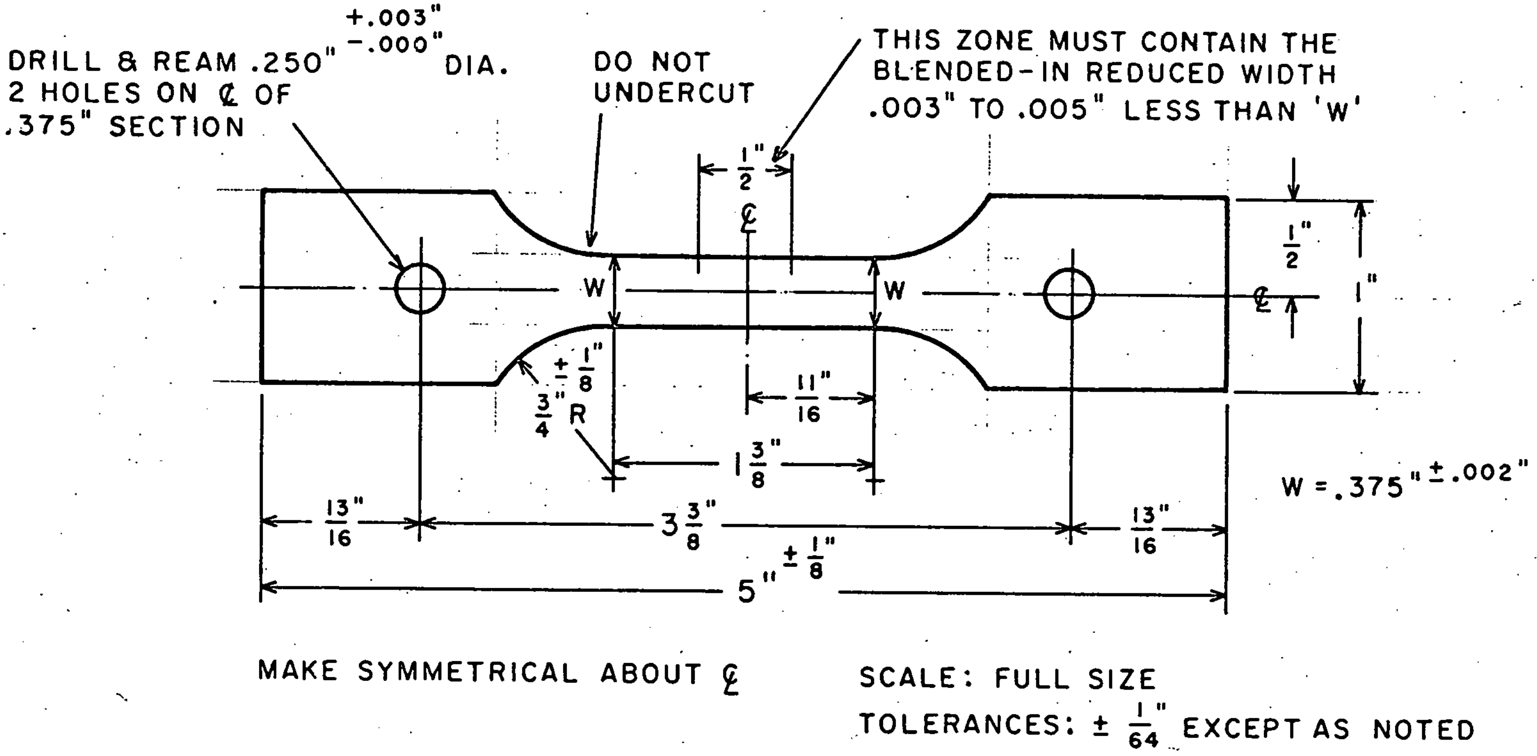

FIG. 2. - UNNOTCHED TENSILE AND DELAYED FAILURE SPECIMEN.

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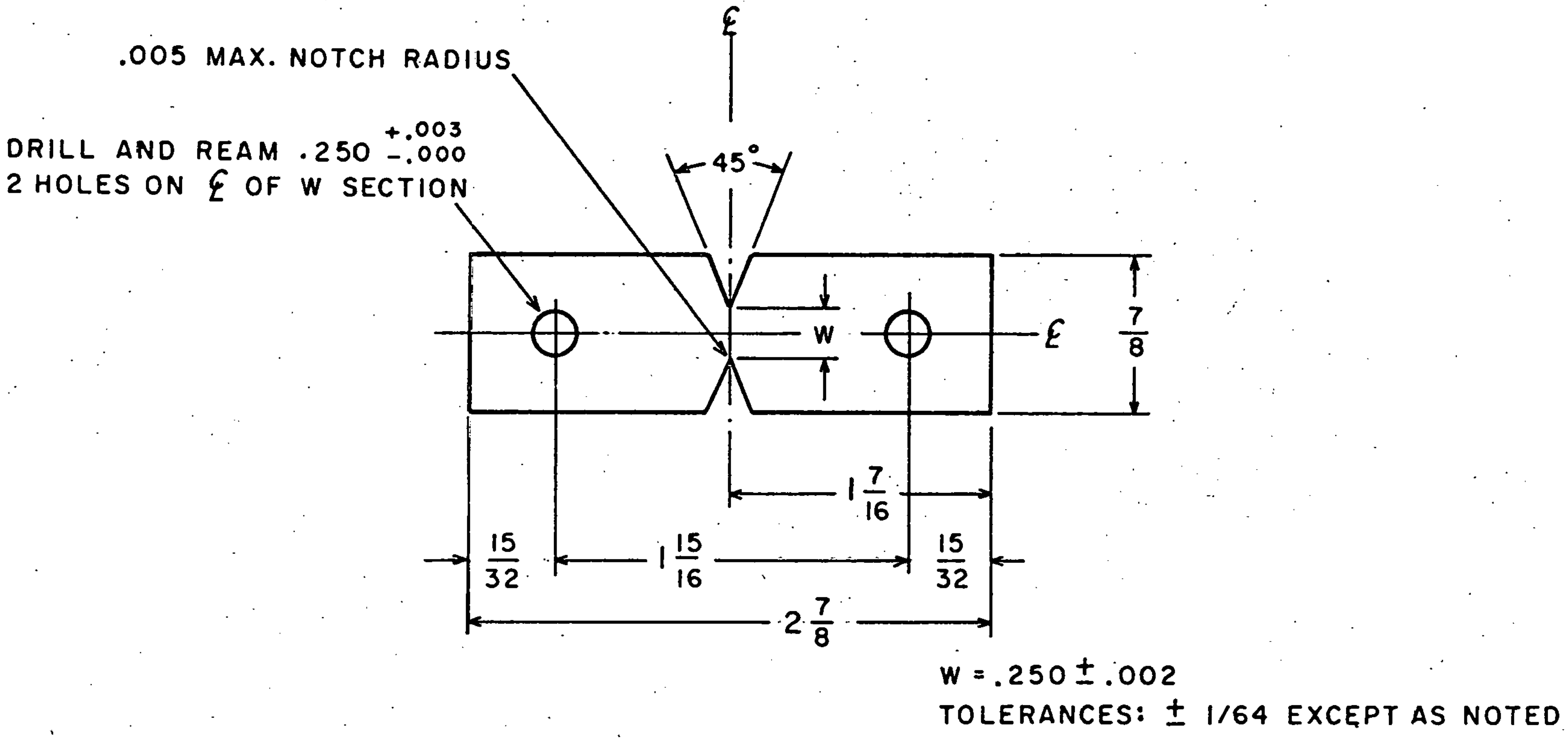
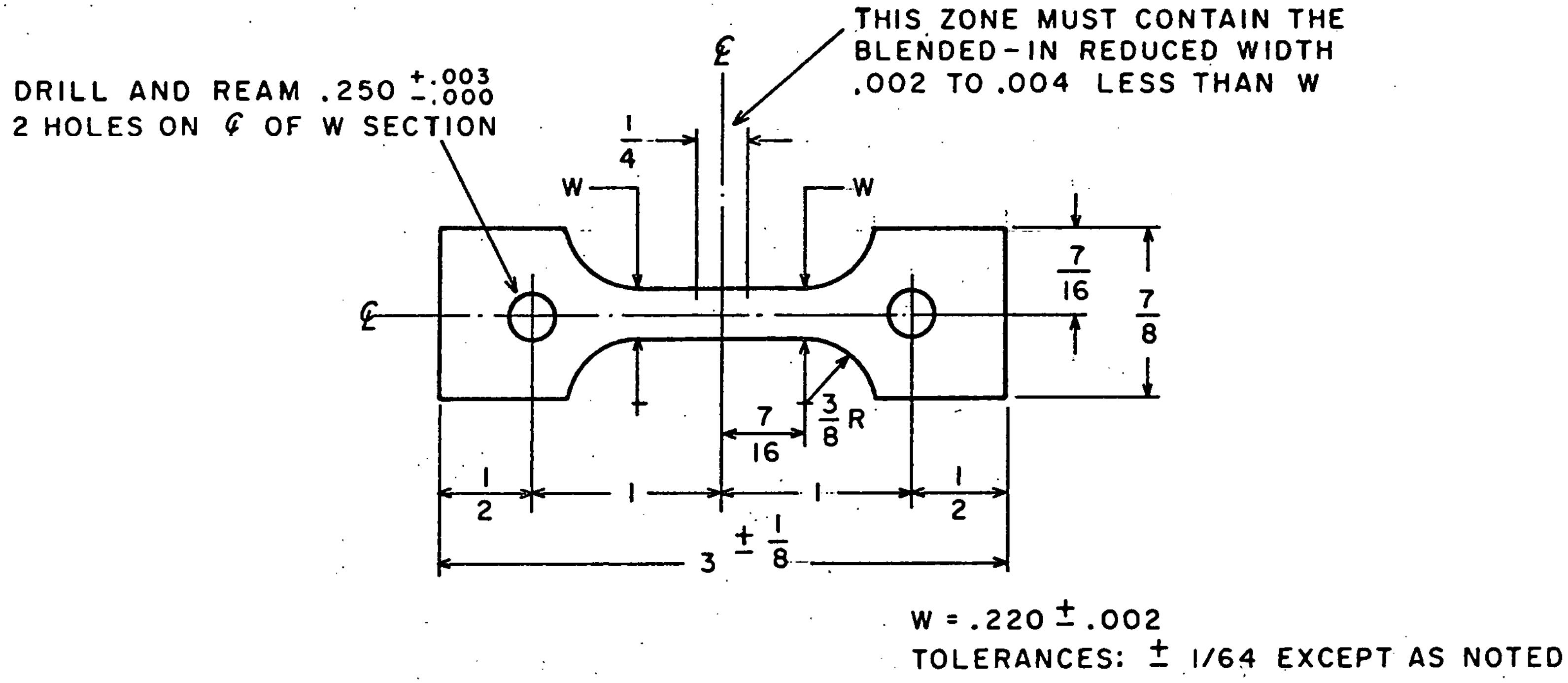


FIG. 3 - REDUCED SIZE NOTCHED TENSILE AND DELAYED FAILURE SPECIMEN.


DRILL AND REAM .250 $^{+.003}_{-.000}$
2 HOLES ON ℄ OF W SECTION

THIS ZONE MUST CONTAIN THE
BLENDED-IN REDUCED WIDTH
.002 TO .004 LESS THAN W

W = .220 ± .002
TOLERANCES: ± 1/64 EXCEPT AS NOTED

FIG. 4 - REDUCED SIZE UNNOTCHED TENSILE AND DELAYED FAILURE SPECIMEN.

After the specimens were machined, they were cleaned by pickling very lightly in a $5HF-45HNO_3-50H_2O$ solution followed by rinsing in warm tap water and ethyl alcohol. Lint-free gloves were used in handling these materials so as to prevent surface contamination which might adversely affect the Sieverts hydriding operation.

Figure 5 is a schematic representation of the modified Sieverts apparatus used for hydrogenation of zirconium specimens. By means of various manometers, vacuum lines, and a calibrated gas burette, this unit essentially allows for measuring out, isolating, and introducing a predetermined quantity of hydrogen to give the desired composition in a specimen of a given weight. In hydrogen charging, the specimen is first vacuum-annealed (approximately 0.02 micron) for one hour at 800°C within the reaction vessel; as this temperature is maintained, the predetermined amount of hydrogen (obtained from thermal decomposition of titanium hydride) is introduced to the specimen, and the absorption is completed within five minutes. The specimen is held at 800°C for an additional 30 to 60 minutes and then slowly cooled. The quantity of hydrogen in the calibrated gas burette at a given temperature is indicated by the manometer pressure reading, and the completion of hydrogen absorption into the specimen is determined by the manometer coming to an equilibrium value.

When hydrogen charging is performed to the 200 ppm level, vacuum fusion analysis has shown that an accuracy of about 10 per cent is obtained. At higher hydrogen levels, the accuracy improves to less than 5 per cent and weight change can be employed for checking the hydrogen content. To check the 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 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

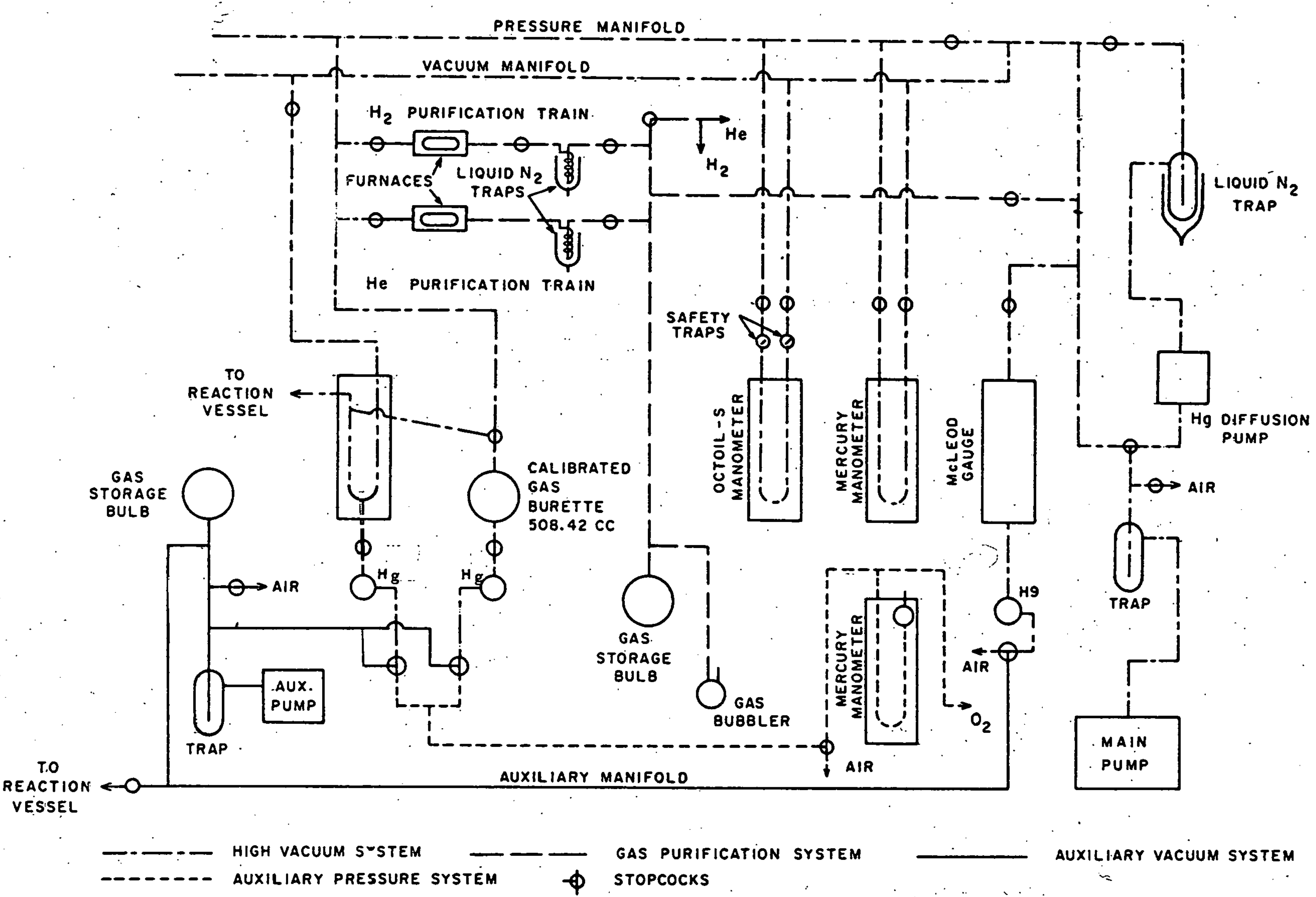


FIG. 5 - SCHEMATIC DIAGRAM OF SIEVERTS APPARATUS.

scatter of data in vacuum fusion analysis, the techniques employed for hydrogenation appear satisfactory.

Following hydrogenation, heat treatment was carried out if necessary or desired. In the case for Zr-2.5Nb, maximum mechanical properties were developed by a heat treatment consisting of annealing at 880°C for 30 minutes followed by water quenching and then aging at 500°C for seven hours.(13) The heat treating response of this alloy can be checked by following hardness changes. The as-received sheet of hot-rolled Zr-2.5Nb had a hardness of 233 VHN; after hydrogenation to the 500 ppm level, the hardness of specimens was in the range 256 to 270 VHN. After quenching from 880°C, the hardnesses were between 271 and 289 VHN and the tempering treatment resulted in an increase to the range 281 to 295. It is apparent that the introduction of hydrogen does not affect the heat-treating response of Zr-2.5Nb. One should note that the hardnesses reported here are about 30 VHN higher than the maximum obtained by Bell and Evans;(13) this increase is probably due to a higher oxygen content, the possibility of slightly higher niobium concentrations, and the introduction of 500 ppm hydrogen.

The as-machined notched specimens have a notch radius of not less than 0.004 inch; after pickling, this radius is somewhat increased and is larger than desired. Initially, a knife-edged, hardened steel tool was depressed into the notch; this resulted in a radius of about 0.001 inch and a theoretical stress concentration factor K_t of 10. However, a severely cold-worked region resulted in the area around the notch, and such a condition was deemed unsatisfactory. A more acceptable method of reducing the notch radius was to employ a 0.001 inch diameter tungsten wire immersed in oil containing fine alumina. The wire moves continuously in the base of the notch and "wears in" a 0.001 inch wide slot to a depth of about 0.003 to 0.005 inch. Rounding of the specimen edges was prevented by maintaining a constant tension on the wire, and the resulting notch radius was somewhat less than 0.001 inch. The configuration of a 0.001 inch slot superimposed on a notch of about 0.005 inch radius results in a theoretical stress concentration factor less than 10; however, the K_t is not lower than 8. No cold-worked area surrounding the notch was obtained by this procedure.

Specimens were evaluated in dynamic tension, to determine first the ultimate tensile strength, and were then tested for delayed failure susceptibility. Tensile tests were carried out on a 10,000-pound capacity Instron machine, and static fatigue evaluation was performed on lever-arm creep/stress-rupture stands which were previously calibrated.

III. RESULTS AND DISCUSSION

A. Unalloyed Zirconium

The microstructure of unalloyed zirconium hydrogenated to the 200 ppm level is shown in Figure 6. The zirconium hydride exists as platelets heavily concentrated in the grain boundaries; only a small amount of hydride aciculae exist within the grains precipitated along habit planes(14)(or twin planes in this case). For material containing 500 ppm hydrogen, the other level studied here, the microstructure is not appreciably changed.

Prior to delayed failure evaluation, the dynamic tensile properties of notched and unnotched zirconium, as-received/vacuum annealed and in the hydrogenated conditions, were determined. The results of this evaluation are presented in Table II and are schematically depicted in Figure 7. For unnotched specimens, one notes that the tensile strength very gradually decreases, the yield strength increases, and the elongation rapidly decreases as the hydrogen content increases to 500 ppm. These data are in general agreement with those of Mehan and Wiesinger;(15) however, the data of Burton(16) show an increase of tensile strength and decrease of yield stress with hydrogen contents up to 500 ppm. The latter work showed a decrease in tensile strength above this hydrogen level and once again an increase at higher concentrations. The effect of hydrogen on total elongation agrees well with Burton's work. The effect of a notch is more easily seen in Figure 7; in the vacuum-annealed condition, the notched tensile strength is higher than the unnotched specimen signifying that zirconium is insensitive to notches under these conditions of low hydrogen content and slow strain rate. As the hydrogen level is increased, the notched tensile strength decreases until, at the 500 ppm level, the notched strength is lower than that of the unnotched condition; such behavior indicates a certain notch sensitivity, although relatively mild in this case. Mehan and Wiesinger(15) have observed this behavior for only coarse-grained material.

Neg. No. 22352 Mag. X500

Fig. 6

Microstructure of unalloyed zirconium containing approximately 200 ppm hydrogen. Zirconium hydride aciculae are concentrated in the grain boundaries.
Etchant: 1HF-1HNO_3-3 Glycerin.

TABLE II

DYNAMIC TENSILE PROPERTIES OF UNALLOYED ZIRCONIUM AT ROOM TEMPERATURE

Condition	Ultimate Tensile Strength, psi	Yield Stress, psi (0.2% offset)	Total Elongation, %
Unnotched, vacuum-annealed	51,000	19,200	32.5
Unnotched, 200 ppm H_2	51,400	21,200	27.3
Unnotched, 500 ppm H_2	48,300	21,700	24
Notched, vacuum-annealed	55,100	28,700	(6.7)*
Notched, 200 ppm H_2	51,900	28,700	(4.2)*
Notched, 500 ppm H_2	45,200	27,100	(2.5)*

* Values taken from load-extension curve; deformation confined to area around base of the notch.

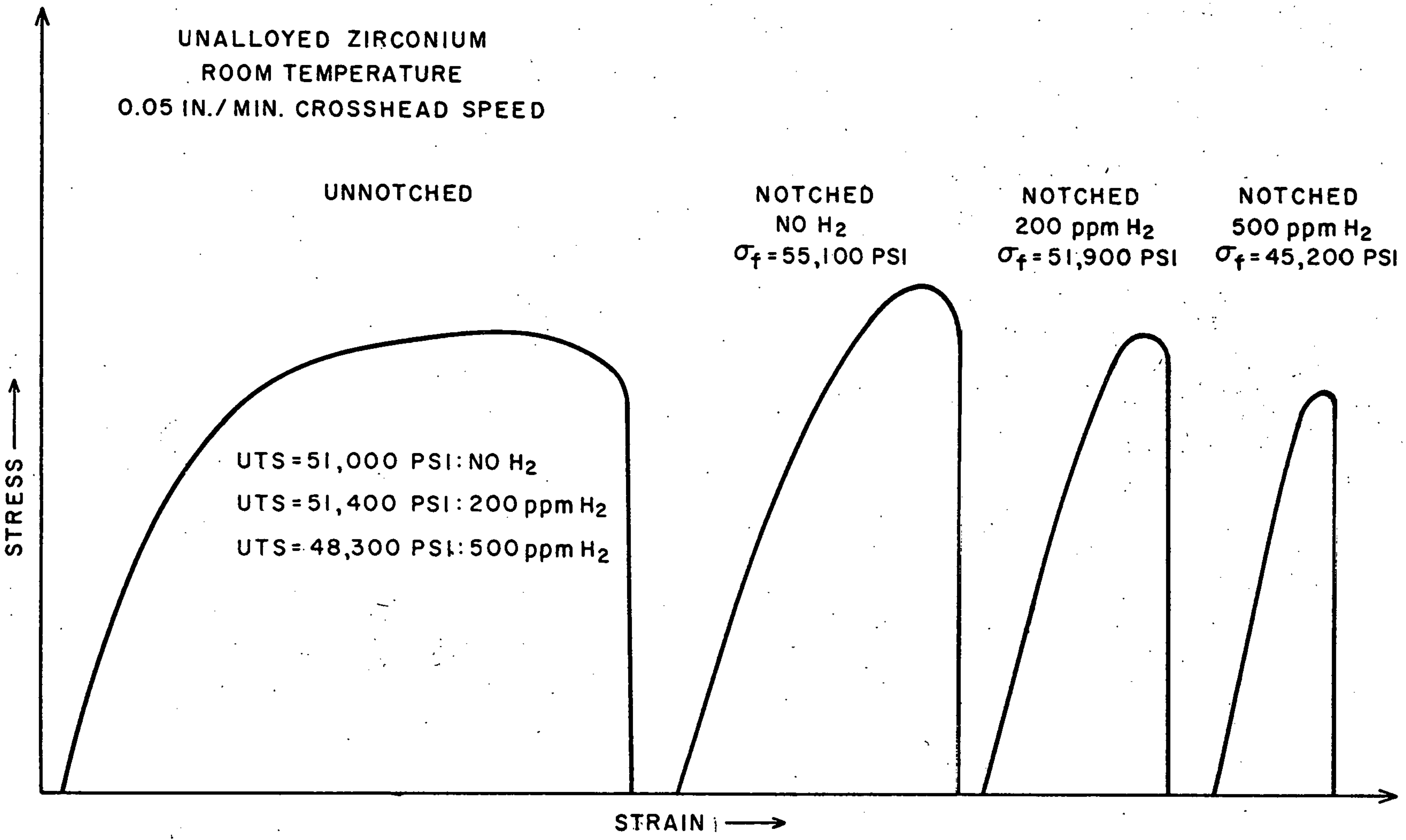


FIG. 7 - DYNAMIC TENSILE BEHAVIOR OF UNALLOYED ZIRCONIUM.

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The above tensile data, while certainly of interest per se, were obtained and served mainly for the purpose of defining the range of applied stresses to be used for delayed failure evaluation. The results of static fatigue tests on unnotched zirconium specimens containing 200 ppm hydrogen and on notched specimens containing 200 ppm and 500 ppm hydrogen are presented in Table III. Inspection of these data reveal that at high stress levels failure occurred at rather short times; at applied stresses approximately 10, 000 psi below the ultimate tensile strength, no fractures occurred within the arbitrarily chosen maximum test duration of 1000 hours. Moreover, the mechanism of failure is not known with certainty, but one might expect the mode of fracture to be creep. Increasing the hydrogen content to 500 ppm did not cause an increase in susceptibility to delayed failure of unalloyed zirconium; at an applied stress of about 8, 000 psi below the ultimate strength, fracture did not occur within 1000 hours.

The behavior of unalloyed zirconium in static tests can be compared to the fracture characteristics of titanium(3) and steel(1) when subjected to static fatigue; such a comparison is represented schematically by the curves shown in Figure 8. The behavior of zirconium is depicted by curve A and is obviously not characteristic of the known behavior of either titanium (B) or steel (C). One concludes, therefore, that unalloyed zirconium containing up to 500 ppm hydrogen is relatively insensitive to delayed failure at room temperature.

B. Zircaloy-2

The microstructure of Zircaloy-2 hydrogenated to the 200 ppm level is shown in Figure 9. The zirconium hydride phase exists as aciculae concentrated primarily in grain boundaries; the Zr-Sn-Fe intermetallic compound ordinarily found in Zircaloy-2 is also observed in the microstructure. At 500 ppm hydrogen, the grain boundaries are more heavily loaded with hydride platelets and more hydride exists on specific crystallographic planes within the grains. There is no essential difference between this microstructure and the one for unalloyed zirconium (Figure 6) with regard to morphology and existence of hydrides.

TABLE III

SUMMARY OF DELAYED FAILURE EVALUATION OF UNALLOYED ZIRCONIUM AT ROOM TEMPERATURE

Applied Stress, psi	Time to Failure, hr
	Unnotched, 200 ppm H_2
43,500	6
41,500	49.5
39,500	129.6
36,000	no failure within 1000 hr
30,000	no failure within 1000 hr
27,000	no failure within 1000 hr
25,000	no failure within 1000 hr
20,000	no failure within 1000 hr
	Notched, 200 ppm H_2
47,900	0.1
44,200	22.3
40,400	no failure, 1458 hr
37,200	no failure, 1458 hr
31,900	no failure, 1316 hr
26,600	no failure, 1149 hr
	Notched, 500 ppm H_2
45,500	instantaneous
41,500	0.3
37,250	no failure, 1081 hr

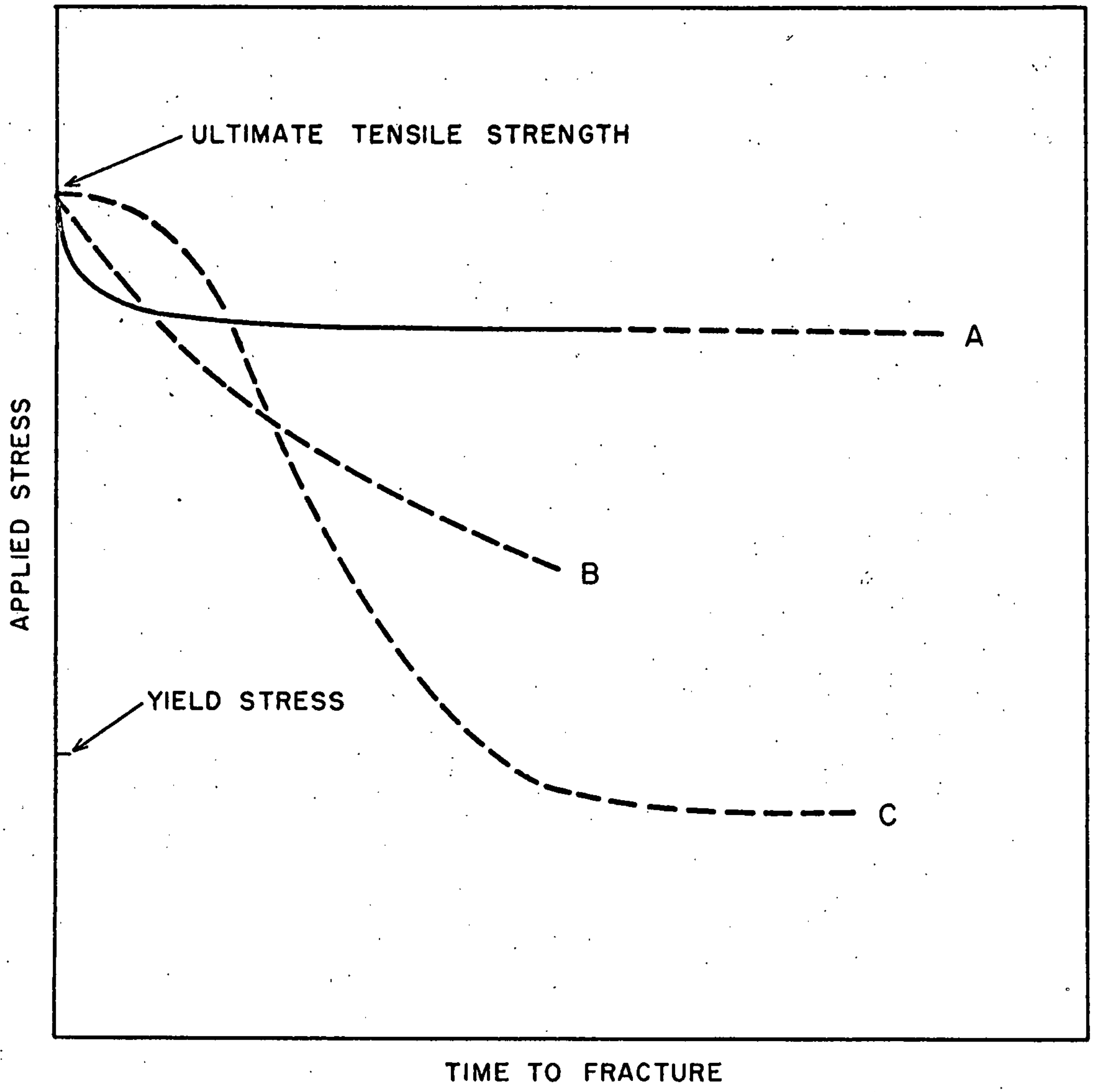

FIG. 8 - SCHEMATIC REPRESENTATION OF STATIC FATIGUE TESTS ON VARIOUS MATERIALS CONTAINING HYDROGEN.

A. Unalloyed Zirconium - This Investigation
B. Some Titanium Alloys
C. High-Strength Steels

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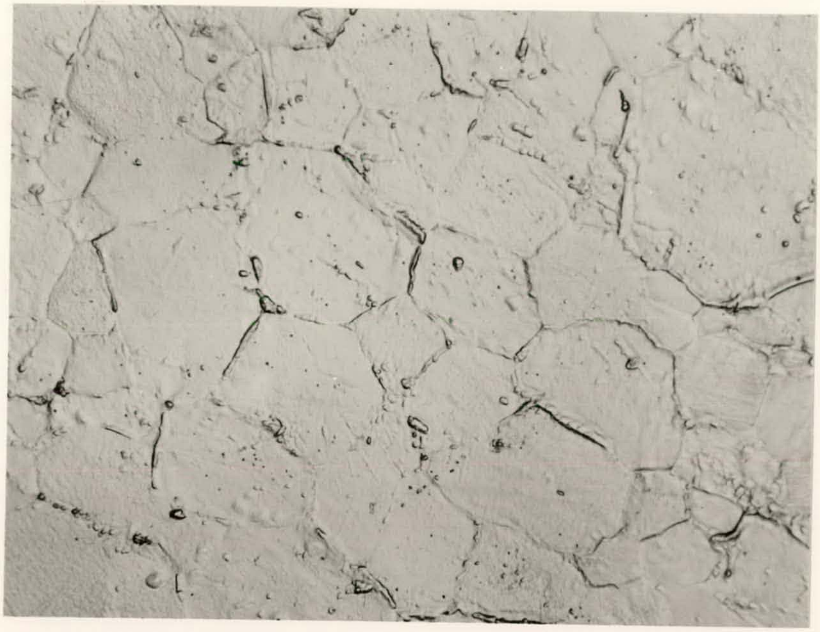

Neg. No. 22353 Mag. X500

Fig. 9

Microstructure of Zircaloy-2 containing 200 ppm hydrogen. Hydrides are present as platelet phase concentrated primarily in grain boundaries.
Etchant: $1HF-1HNO_3-3$ Glycerin.

The dynamic tensile properties of the three lots of Zircaloy-2 were determined for the purpose of defining the range of applied stress to be used in delayed failure evaluation. The results are presented in Table IV for notched and unnotched specimens in the vacuum-annealed and hydrogenated condition; a general schematic representation of these data is shown by the stress-strain curves in Figure 10. In general, the effect of hydrogen and notches on Zircaloy-2 is similar to the effects already outlined for unalloyed zirconium. That is, increased hydrogen contents increase the unnotched tensile strength and decrease the elongation; the fracture strength in the notched condition, however, decreases as the level of hydrogen content becomes greater. Apparently, the notch sensitivity is greatly increased with higher hydrogen levels; in fact, at 500 ppm hydrogen notched specimens show no plasticity and fracture occurs in the elastic portion of the stress-strain curve. Such a specimen might have an increased susceptibility for delayed failure due to the greater amount of strain energy stored in the specimen which is available for crack propagation.

A summary of delayed failure studies on the three lots of Zircaloy-2 is presented in Table V. The behavior of notched and unnotched specimens with 200 ppm or 500 ppm hydrogen is essentially the same as unalloyed zirconium--failure occurs only at high stress levels (at or very near to the ultimate tensile strength). A static fatigue curve for this material would be similar to the schematic curve for unalloyed zirconium (curve A) in Figure 8. Apparently, a notch-sensitive condition (Lot B and Lot R, 500 ppm H_2) where fracture occurs in the absence of macroscopic plastic deformation does not promote the occurrence of delayed failure in this material to any great extent. One concludes, therefore, that notched and unnotched Zircaloy-2 containing 200 ppm and 500 ppm hydrogen is not susceptible to delayed failure at room temperature.

The conflict of results between those obtained here and those of Ostberg(7) is apparent. His work has shown that Zircaloy-2 behaves in a manner similar to titanium (Figure 8), whereas no evidence for delayed failure in this material has been indicated in the present investigation. However, Ostberg has observed delayed failure in only one lot of Zircaloy-2; for other sources of this material, no static fatigue failure has occurred.

TABLE IV

DYNAMIC TENSILE PROPERTIES OF ZIRCALOY-2 AT ROOM TEMPERATURE

Condition	Ultimate Tensile Strength, psi	Yield Stress, psi (0.2% offset)	Total Elongation, %
		LOT W	
Unnotched, vacuum-annealed	45,300	32,000	41.5
Unnotched, 200 ppm H_2	47,100	31,800	34.5
Unnotched 500 ppm H_2	63,200	39,600	33
Notched, vacuum-annealed	64,200	44,300	(10.9)*
Notched, 200 ppm H_2	62,200	41,800	(6.2)*
Notched, 500 ppm H_2	58,800	47,300	(4.2)*
		LOT B	
Unnotched, vacuum-annealed	60,300	---	---
Unnotched, 200 ppm	64,600	44,100	33.7
Unnotched, 500 ppm	71,800	49,100	28.9
Notched, vacuum annealed	84,400	---	---
Notched, 200 ppm	78,300	62,800	(3.5)*
Notched 500 ppm	63,400**	---**	(2.7)*

TABLE IV (continued)

Condition	Ultimate Tensile Strength, psi	Yield Stress psi (0.2% offset)	Total Elongation %
	LOT R		
Unnotched, vacuum-annealed	74,100	65,000	30.6
Unnotched, 500 ppm	77,900	59,900	26.6
Notched, vacuum-annealed	96,700	86,800	(4.7)*
Notched, 500 ppm	59,800**	---**	(1.8)*

* Values taken from load-extension curve; deformation confined to area around base of the notch.

** Load-extension curve showed straight line to fracture.

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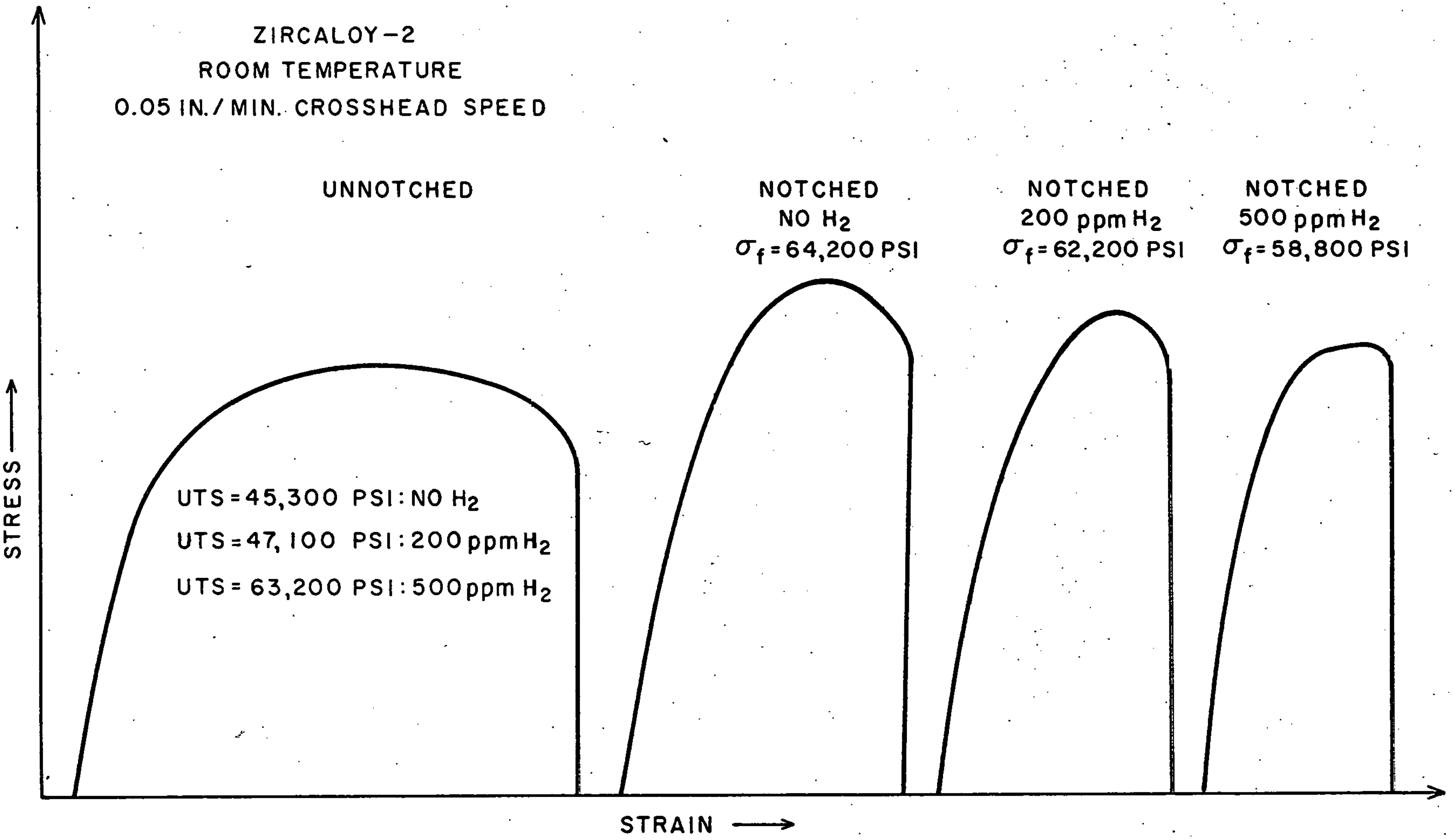


FIG. 10 - SCHEMATIC REPRESENTATION OF DYNAMIC TENSILE PROPERTIES OF ZIRCALOY-2.

TABLE V

SUMMARY OF DELAYED FAILURE EVALUATION OF ZIRCALOY-2 AT ROOM-TEMPERATURE

Applied Stress, psi	Time to Failure, hr
Lot W, Unnotched, 200 ppm H_2	
47,400	no failure, 1103 hr
45,700	no failure, 1103 hr
44,000	no failure, 1103 hr
41,250	no failure, 1103 hr
38,700	no failure, 1103 hr
30,400	no failure, 1103 hr
Lot W, Notched, 200 ppm H_2	
68,000	2.75
60,600	no failure, 1000 hr
59,500	no failure, 1292 hr
55,400	no failure, 1290 hr
52,100	no failure, 1146 hr
47,800	no failure, 1146 hr
40,400	no failure, 1146 hr
Lot W, Notched, 500 ppm H_2	
58,500	no failure, 1266 hr
55,400	no failure, 1266 hr
51,000	no failure, 1266 hr
45,500	no failure, 1266 hr
41,500	no failure, 1266 hr
37,250	no failure, 1266 hr

TABLE V (continued)

Applied Stress, psi	Time to Failure, hr
Lot B, Notched, 500 ppm H_2	
62, 200	0. 02
60, 000	0. 02
56, 700	0. 02
52, 200	no failure, 928 hr
46, 700	no failure, 928 hr
Lot R, Notched, 500 ppm H_2	
58, 000	0. 02
53, 000	0. 02
47, 000	no failure, 1000 hr
40, 000	no failure, 1000 hr
30, 000	no failure, 1000 hr

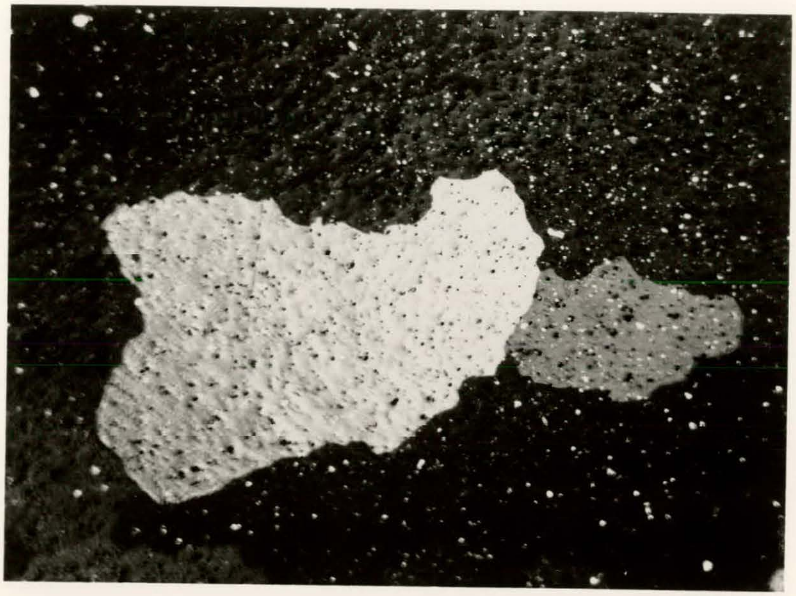
Apparently, he has no explanation for this behavior, and he has not been able to correlate his results with any particular parameter--such as composition or prior metallurgical history.

Mehan and Wiesinger(15) have reported that large-grained Zircaloy-2 containing 500 ppm hydrogen is more notch sensitive than fine-grained material. To study the effect of an increased grain size on susceptibility of Zircaloy-2 to delayed failure, sheet material was prestrained 7 per cent (in tension) and annealed at 800° C for 65 hours. The resulting grain size is shown in Figure 11; it is very much larger than material simply vacuum-annealed at 800° C. Dynamic tensile tests of unnotched, coarse-grained specimens showed a sharp drop in ductility with or without 500 ppm hydrogen. A slight drop of tensile strength was observed for specimens without hydrogen, and a 10, 000 psi reduction of ultimate strength was observed for large-grained material with 500 ppm hydrogen. In the case of notched specimens, an increase in strength was noted for coarse-grained material with or without hydrogen and a slight decrease in total deformation was obtained for both cases. Thus, we did not observe increased notch sensitivity due to a large grain size.

Notched specimens of this strain-annealed material were hydrogenated to the 500 ppm level and evaluated for delayed failure susceptibility. A summary of applied stress and times to failure is summarized below.

Applied Stress, psi	Time to Failure, hr
59, 000	<0.02
57, 000	<0.02
55, 000	<0.02
52, 000	<0.02
49, 000	1.4
45, 000	No failure, 1342 hr

While failure was observed at a stress approximately 10, 000 psi lower than the tensile strength, the asymptotic behavior of the resulting curve at a rather high stress level indicates no sensitivity to static fatigue under these conditions. Apparently then, a large grain size does not promote delayed failure in Zircaloy-2.



Neg. No. 22561 Mag. X50

Fig. 11

Microstructure of Zircaloy-2 strained 7 per cent and annealed at 800°C for 65 hours, showing an extremely large grain size. Spots are a result of heavy etching and long photographic exposure. Polarized light. Etchant: 1HF-1HNO_3-3 Glycerin.

To study the effect of cold working on static fatigue sensitivity, Zircaloy-2 strip was hydrided to the 200 ppm level and cold-rolled 20 per cent. Notched specimens were prepared, and the dynamic tensile strength of this material was determined as 97,400 psi. A summary of the static fatigue property evaluation is presented below.

Applied Stress, psi	Time to Failure, hr
95,000	<0.02
90,000	<0.02
83,000	<0.02
73,000	No failure, 1006 hr
60,000	No failure, 1006 hr

These data are similar to those previously presented and show that 20 per cent cold reduction by rolling does not markedly increase the susceptibility of Zircaloy-2 to delayed failure at room temperature.

Various investigations were conducted to determine if corrosion in superheated steam would promote delayed failure. In one case, notched Zircaloy-2 specimens were exposed to 750°F steam (1500 psi) for a period of 2016 hours; the hydrogen content of these specimens after steam exposure averaged 130 ppm which is in reasonable agreement with published hydrogen pickup data for this material. Static fatigue tests did not show increased susceptibility to fracture due to the corrosion oxide and high oxygen subsurface. In another experiment designed to determine corrosion effects on delayed failure characteristics, notched specimens were hydrogenated to the 500 ppm level, stressed in a specially designed stainless steel fixture, and then exposed to 750°F steam while under applied stress. After 29 days' exposure, no fractures were observed. The specimens were further evaluated for static fatigue susceptibility at room temperature, and no effect of the prior stress/corrosion test was observed. It appears, therefore, that corrosion does not affect delayed failure characteristics of Zircaloy-2.

To determine if an increased quantity of hydrogen in solution with alpha zirconium would affect delayed failure properties, notched specimens of Zircaloy-2 containing 500 ppm hydrogen were solution-annealed at 600°C for 7 hours followed by water quenching. While the total hydrogen content of the specimen is in solution when in equilibrium at 600°C, only a small fraction of this quantity is retained in solution after quenching; supposedly, only 60 ppm hydrogen remains in alpha zirconium after quenching to room temperature. The ultimate tensile strength was increased by the quenching treatment; however, no change in static fatigue properties of Zircaloy-2 was observed. One would conclude from the foregoing results and discussion that Zircaloy-2 is apparently insensitive to static fatigue and the introduction of cold work, an increased grain size, corrosion in superheated steam, and water quenching do not promote susceptibility to this fracture phenomenon.

C. Zr-1.25Al-1Sn-1Mo

As previously mentioned, the strength of an alloy is an important factor in the phenomenon of delayed failure. If one considers the nucleation of a dislocation crack or small microcrack, one of the more important parameters determining whether or not such a crack will propagate is the strength or toughness of the material. Except in some isolated cases--notably certain high-strength, heat-treated alloy steels--as the strength of an alloy increases, the toughness decreases or the material becomes more notch sensitive and susceptible to crack propagation. It follows, therefore, that unalloyed zirconium and Zircaloy-2--being relatively low-strength alloys--may not be nearly as sensitive to delayed failure as a high-strength zirconium alloy. (Steels below about 75,000 psi ultimate tensile strength, for example, do not exhibit hydrogen embrittlement by delayed failure.)

In the light of this analysis, investigation of a high-strength zirconium alloy, Zr-1.25Al-1Sn-1Mo,* was initiated. The microstructure of this material after hydriding to 500 ppm hydrogen is shown in Figure 12. Initially, the metallographic specimen was etched in the HF-HNO_3-glycerin solution. No hydride, however, could be observed; bringing out hydrides with this etchant is difficult enough, and the fine structure and second phase further complicated the observation. M. L. Picklesimer,(17) has described

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* This material was developed by Atomics International for use in a liquid-sodium cooled reactor at 1200°F. The authors would like to thank Mr. R. K. Wagner, A. I. for providing this material for study herein.

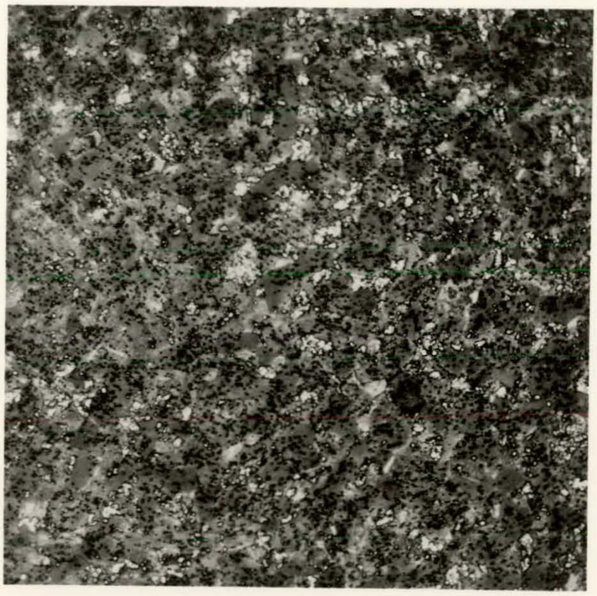

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Fig. 12

Microstructure of Zr-1.25Al-1Sn-1Mo containing 500 ppm hydrogen; anodically etched (see text) such that hydrides appear yellow (white) in a blue (gray) zirconium matrix. Very few hydride aciculae are present but some exist as small round particles. Apparently, some of the hydrogen exists in solution; a second, unidentified phase at grain boundaries, as well as a fine precipitate, exists in the microstructure.

an electrolytic anodic etching technique whereby the anodized surface causes hydrides to be yellow and zirconium to be blue. He has been able to detect as little as 30 ppm hydrogen in Zircaloy-2 by this technique. The solution used in this method is the following:

40 ml glycerin
120 ml absolute ethyl alcohol
70 ml water
20 ml lactic acid (87%)
10 ml conc. orthophosphoric acid
4 g citric acid

Initial work with this solution on unalloyed zirconium and Zircaloy-2 was extremely successful; the hydrides were revealed in very sharp contrast to the matrix. Using this technique for Zr-Al-Sn-Mo, however, revealed only a small amount of yellow, spherical particles (white in photomicrograph)--no aciculae. If one places complete confidence in this technique, and there is good enough evidence to do so, then one must conclude that part of the hydrogen is in solid solution in this alloy. Considering that aluminum and tin have relatively high solubility in zirconium, the quaternary system Zr-Al-Sn-H might show an increased solubility for hydrogen at room temperature.

Prior to delayed failure evaluation, the dynamic tensile properties of Zr-Al-Sn-Mo were determined in the notched and unnotched condition --as-annealed and with 500 ppm hydrogen added. The results of this work are presented in Table VI and are graphically represented by the curves in Figure 13. There are two important observations to be made from these data. First, one must note the extremely high strength of this material--124,000 psi ultimate in the vacuum annealed condition with an increase to 141,000 psi at 500 ppm absorbed hydrogen. Second, the material is highly notch-sensitive; in the vacuum-annealed condition, the notched specimen has a fracture stress lower than the ultimate tensile strength of unnotched specimens and the notched specimen containing 500 ppm hydrogen shows an even lower fracture stress of only 69,400 psi. In the latter specimen, moreover, no deviation from Hooke's law occurs to fracture. Considering the tensile properties of this high-strength alloy, as compared to the tensile behavior of Zircaloy-2, it is fairly clear that crack propagation through Zr-Al-Sn-Mo should be

TABLE VI

DYNAMIC TENSILE PROPERTIES
OF Zr-1.25Al-1Sn-1Mo ALLOY
AT ROOM TEMPERATURE

Condition	Ultimate Tensile Strength, psi	Yield Stress, psi (0.2% offset)	Total Elongation, %
Unnotched, vacuum-annealed	124,000	91,800	13.4
Unnotched, 500 ppm H_2	141,000	102,000	15.6
Notched, vacuum-annealed	121,000	--**	(3.8)*
Notched, 500 ppm H_2	69,400	--**	(2.2)*

* Values taken from load-extension curve; deformation confined to area around base of the notch.

** Fracture occurred within Hooke's law region of stress-strain curve.

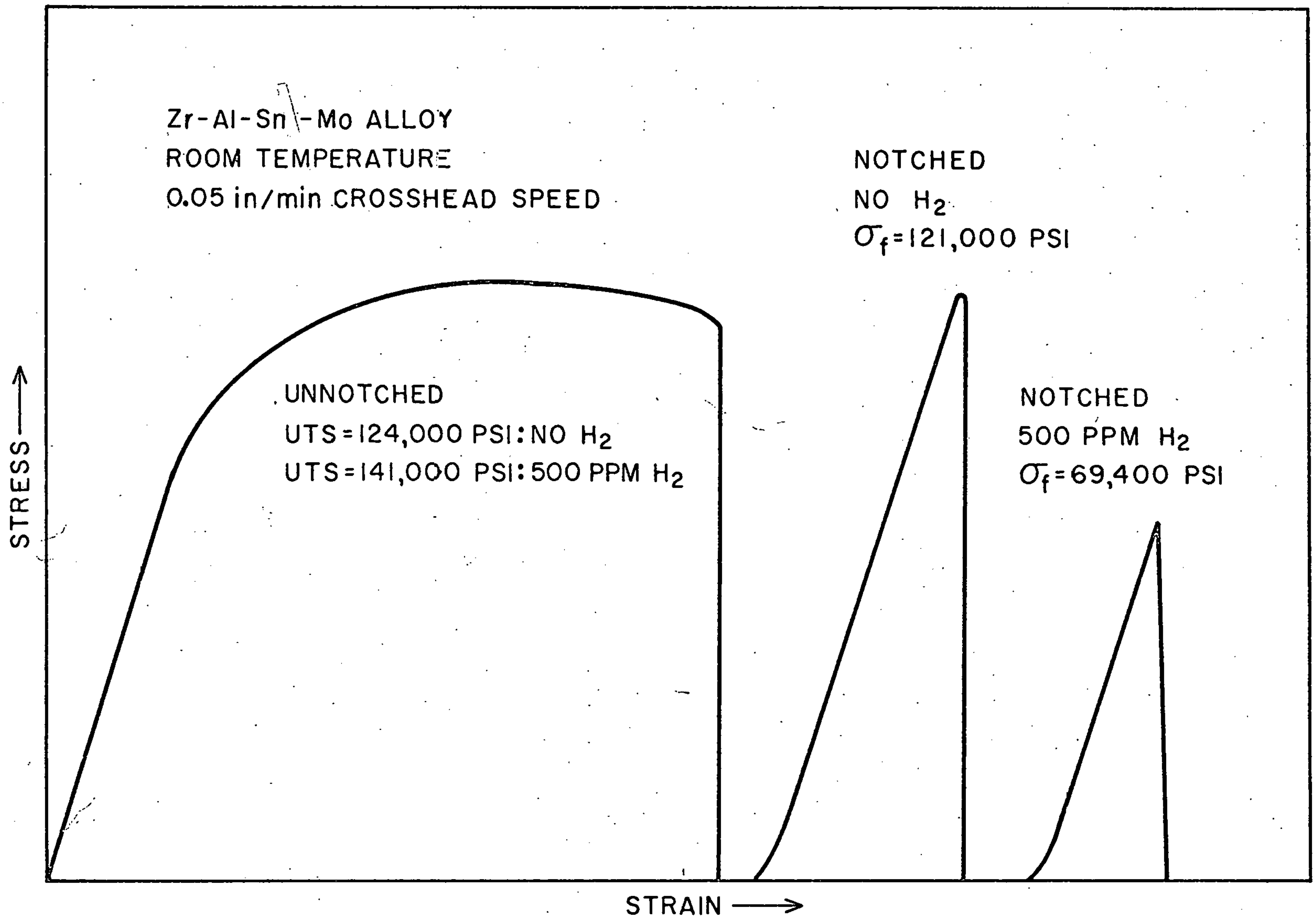

FIG. 13 - SCHEMATIC REPRESENTATION OF DYNAMIC TENSILE PROPERTIES OF Zr-1.25Al-1Sn-1Mo ALLOY.

considerably easier. In fact, the tensile behavior exhibited by this alloy represents optimum conditions for time-dependent, static fatigue failure.

The delayed failure evaluation of Zr-Al-Sn-Mo was performed at room temperature on notched specimens containing 500 ppm hydrogen; applied stresses ranged from 68, 500 psi to 10, 000 psi. A summary of these studies is presented in Table VII, and the results obtained were represented by the curves in Figure 14. It is immediately apparent that the static fatigue characteristics of this material are entirely different from unalloyed zirconium and Zircaloy-2 and closely resemble the static fatigue curve for titanium shown in Figure 8 (curve B). Moreover, the appearance of the fracture surfaces was quite different from Zircaloy-2 or unalloyed zirconium; a matte-like, fibrous fracture was obtained for these materials whereas the Zr-Al-Sn-Mo alloy was of the smooth, cleavage type without evidence of gross plastic deformation. From the static fatigue curve of Figure 14, one notes that after approximately 200 hours, fracture occurred at an applied stress of 21, 000 psi--48, 400 psi below the fracture stress. This increment is considerably greater than that observed for unalloyed zirconium or Zircaloy-2, which did not fracture at stresses less than about 10, 000 psi below the ultimate tensile strength. It appears, therefore, that the Zr-1. 25Al-1Sn-1Mo alloy at room temperature under the influence of a notch and containing 500 ppm hydrogen, is very susceptible to delayed failure.

To further substantiate these data and confirm the existence of time-dependent fracture as due to hydrogen absorption, notched specimens were vacuum-annealed in the Sieverts apparatus; however, no hydrogenation was performed. Room-temperature static fatigue tests were carried out at the following applied stress levels:

90, 000 psi
64, 000 psi
59, 000 psi
43, 000 psi

After 695 hours at stress, <u>no</u> fractures had occurred--even in a specimen loaded (90, 000 psi) above the fracture stress of material with hydrogen. (Without hydrogen, the stress of 90, 000 psi is 30, 000 psi below the fracture stress of notched specimens, which is still within the 48, 400 psi increment

TABLE VII

SUMMARY OF DELAYED FAILURE EVALUATION OF NOTCHED Zr-Al-Sn-Mo SPECIMENS CONTAINING 500 PPM HYDROGEN

Applied Stress, psi	Time to Failure, hr
68,500	< 0.02
66,500	< 0.02
64,000	< 0.02
61,000	0.8
59,000	6.1
57,000	4.9
55,000	4.1
52,000	2.1
48,000	8.2
43,000	15.4
40,000	13.7
36,000	30.4
29,000	77.8
26,000	64.3
21,000	202.6
16,000	no failure, 1150 hr
10,000	no failure, 1150 hr

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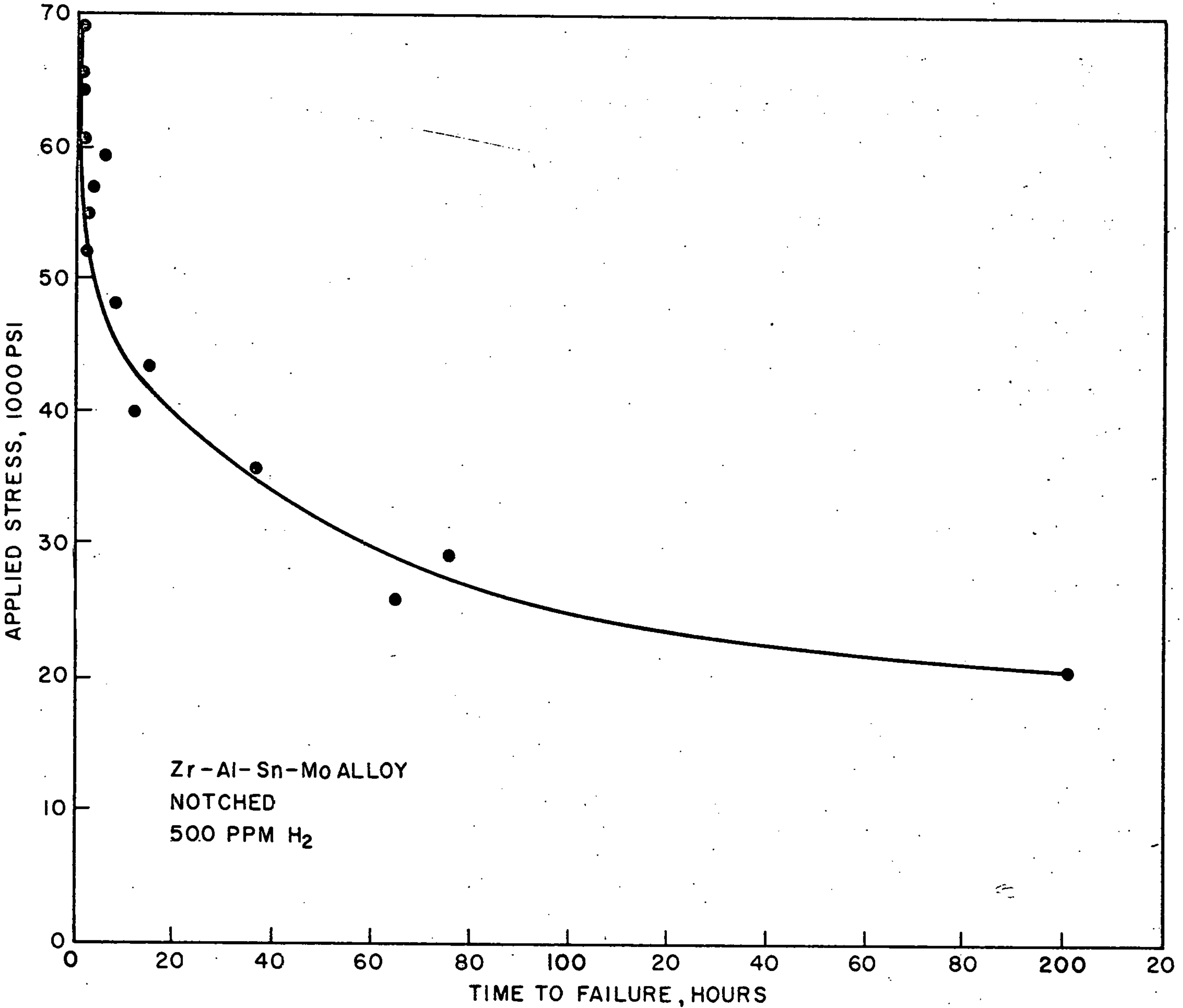

FIG. 14 - DELAYED FAILURE EVALUATION OF Zr-1.25Al-1Sn-1Mo EXPERIMENTAL ALLOY AT ROOM TEMPERATURE.

where failure occurs in hydrogen-containing specimens.) These data show, therefore, that the occurrence of time-dependent, delayed failure in Zr-1.25Al-1Sn-1Mo is definitely due to hydrogen absorption, and fracture is not associated with a creep phenomenon. (If anything, the existence of hydrides would improve creep strength.)

Unnotched specimens of this material were also hydrogenated to the 500 ppm level and evaluated for delayed failure at room temperature. The data obtained are presented in Table VIII, and the static fatigue curve is shown in Figure 15. As in the case for notched specimens, this material in the unnotched condition is relatively susceptible to delayed failure. Fractures occurred as low as 100,000 psi which is 41,000 psi below the ultimate tensile strength; moreover, fracture occurred below the yield stress (102,000 psi) which commonly occurs in hydrogen embrittlement of steel. The shape of the curve in Figure 15 is similar to the static fatigue curves ordinarily obtained for titanium (Figure 8, curve B).

Since the time-dependent fracture characteristics of Zr-Al-Sn-Mo are well defined by delayed failure curves, this material readily allows for determining the effect of common variables on susceptibility to fracture. For example, one may pick a particular stress level, vary a particular parameter, and note the change in time to failure; by testing only a single specimen, at least a cursory determination on the effect of a particular parameter on delayed failure can be obtained.

In determining hydrogen embrittlement in steel, very often the tensile elongation or reduction in area of hydrogen-charged material is plotted as a function of temperature. Normally, a drop in ductility is observed at temperatures much above the transition temperature for uncharged material; it has been shown,(18) in fact, that the curve goes through a minimum, and an increase in ductility is again observed at some low temperature. In addition, the magnitude and position of the minimum is a function of hydrogen content and strain rate. Evidence for possibly the same behavior in hydrogenated zirconium has been provided by data of Burton.(16) Figure 16 is a replot of his data showing per cent reduction in area as a function of temperature for Zircaloy-2 of various hydrogen contents. Notice that for material with 1000 ppm hydrogen, the ductility drops off at approximately

TABLE VIII

SUMMARY OF DELAYED FAILURE EVALUATION OF UNNOTCHED Zr-Al-Sn-Mo SPECIMENS CONTAINING 500 PPM HYDROGEN

Applied Stress, psi	Time to Failure, hr
137,000	0.1
132,000	2.5
125,000	50.7
110,000	146.8
100,000	384.4
85,000	no failure, 1107 hr

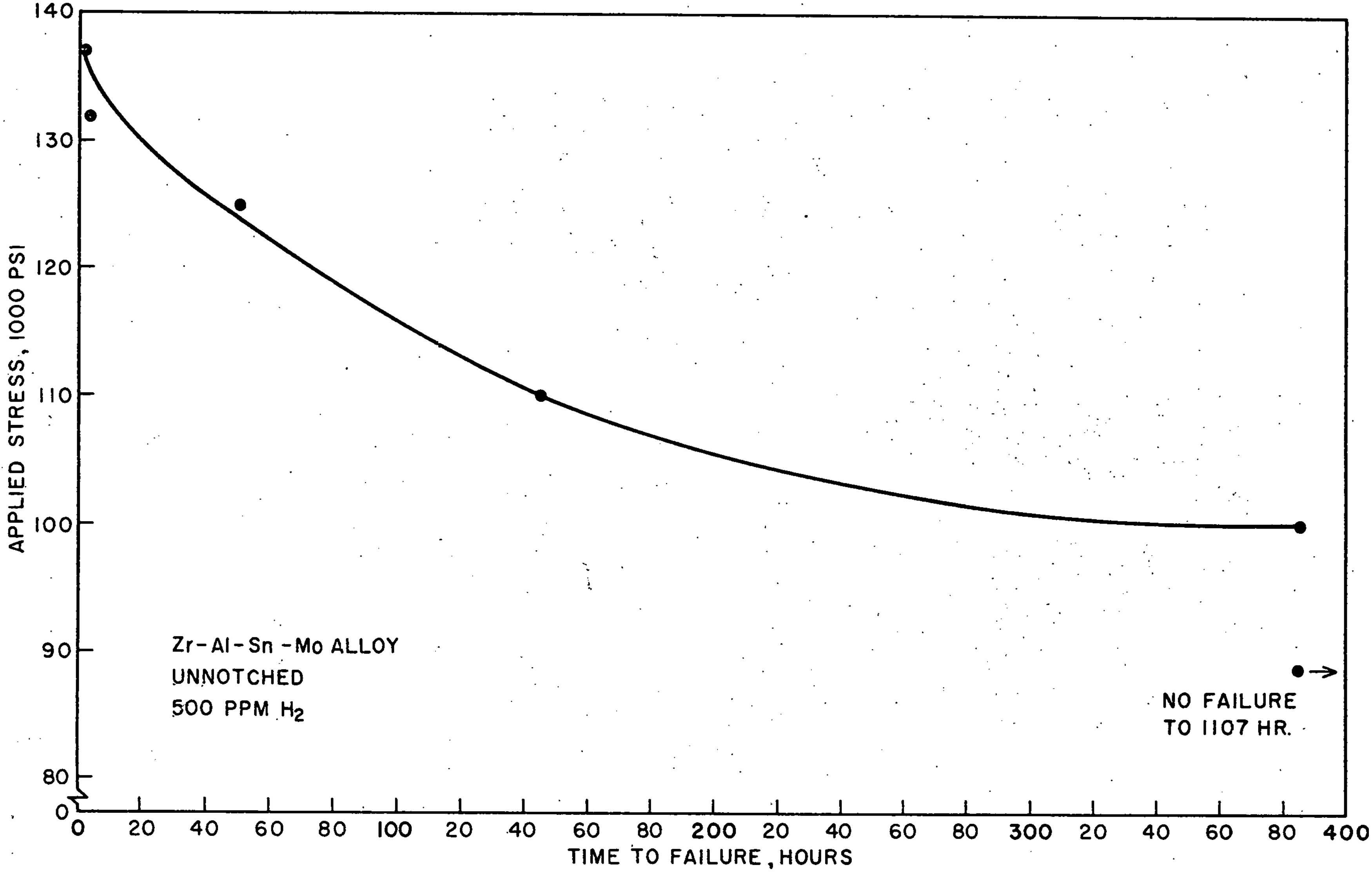

FIG. 15 - DELAYED FAILURE EVALUATION OF Zr-1.25Al-1Sn-1Mo EXPERIMENTAL ALLOY AT ROOM TEMPERATURE.

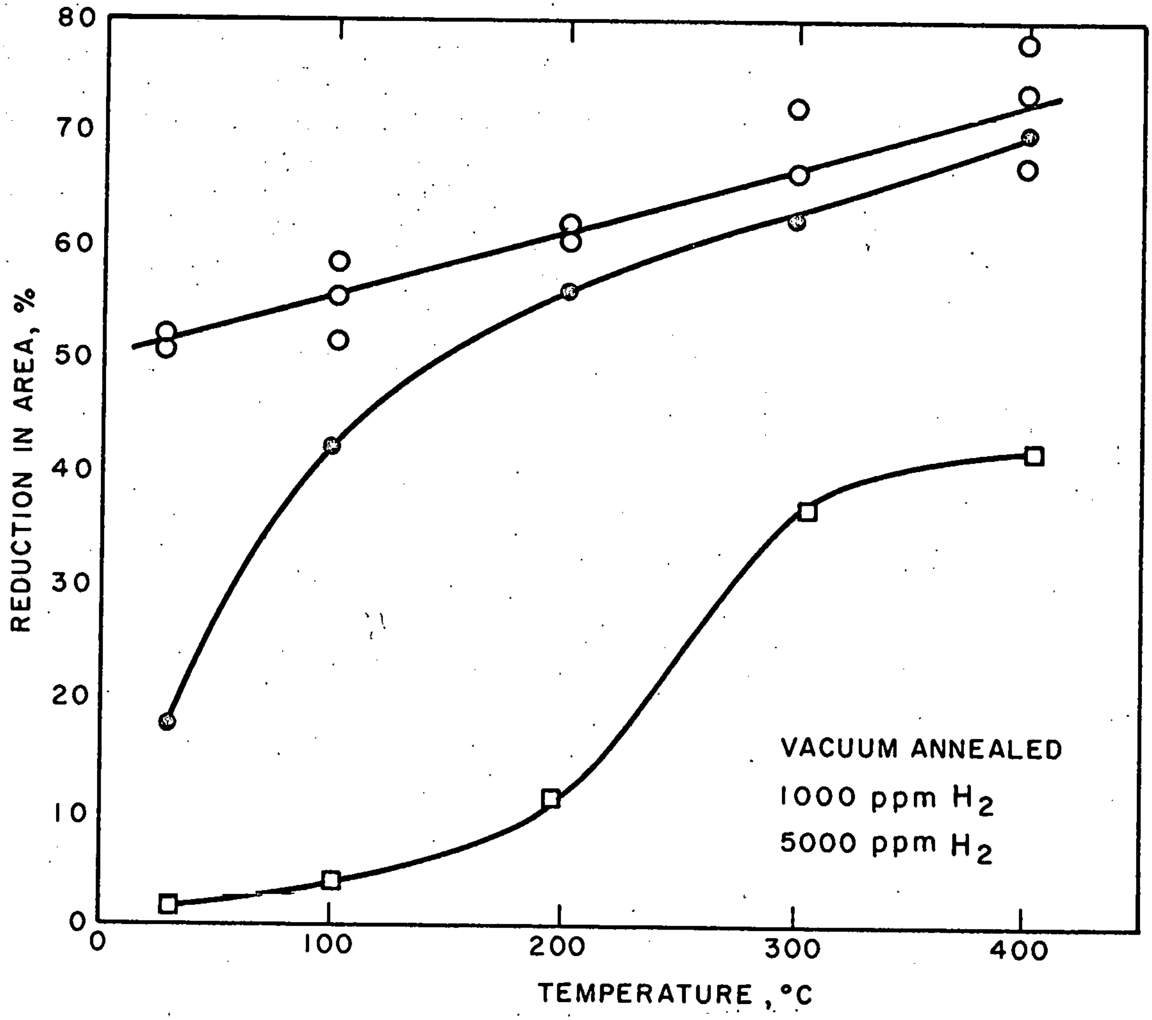

FIG. 16 - PER CENT REDUCTION IN AREA OF ZIRCALOY-2 AS A FUNCTION OF TEMPERATURE.

200° C and decreases rapidly to room temperature; no tests were performed at sub-atmospheric temperatures, and it is not known whether ductility is recovered.

The significance of these curves is that this behavior of ductility versus temperature indicates some interaction between dislocations and interstitial hydrogen--just as in the case for hydrogen-charged steel. One explanation of the mechanism might be the following. As the temperature is lowered, the mobility of hydrogen decreases and tends to occupy the dislocations and create a drag; the minimum is the temperature at which the mobility of hydrogen is just sufficient to keep up with the moving dislocation. At temperatures below this, once the dislocation breaks from its atmosphere, it is free to move without drag from hydrogen atoms and increased ductility is observed.

From the above analysis, it follows that the degree of susceptibility of zirconium to delayed failure should be temperature dependent. From Table VIII, an unnotched specimen of Zr-Al-Sn-Mo at room temperature containing 500 ppm hydrogen will fracture at 2.5 hours when stressed to 132,000 psi. A very simple apparatus was constructed to hold liquid nitrogen (-196° C) around an identical specimen while being stressed at 132,000 psi; <u>no</u> fracture was observed before 2.5 hours, and the test was terminated after 6 hours due to difficulty in maintaining this atmosphere overnight. Another specimen with 500 ppm hydrogen was then evaluated in an ice/water bath at 0° C and at the same applied stress; fracture occurred in <u>0.3 hr</u>. These conditions were repeated on another identical specimen and fracture occurred in <u>0.17 hr</u>. While these data are considered cursory, they do indicate that there is a temperature dependence for delayed failure occurrence and that the curve of fracture time as a function of temperature apparently goes through a minimum. If one accepts these conclusions, it follows that one cannot say that zirconium or Zircaloy-2 is not susceptible to delayed failure; it is simply a matter of degree or magnitude of susceptibility, since certain conditions--as outlined here--tend to promote static fatigue.

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D. Zr-2.5Nb

In development of a pressurized water reactor, Atomic Energy of Canada Limited has considered the use of Zr-2.5Nb--or a slight modification of this alloy--as pressure tube material. Since this component is designed for relatively long-time service and since the tensile strength is considerably greater than that of Zircaloy-2, evaluation of delayed failure susceptibility was performed.

In all cases, specimens were studied in the heat-treated condition so that maximum properties could be developed. Hydrogenation to the 500 ppm level was carried out prior to heat treatment as previously described; the microstructure of this material is shown in Figure 17 for which the anodic etching technique already described was used. At 880° C, the annealing temperature, the material is in the alpha plus beta region; on quenching, therefore, the microstructure consists of primary alpha (shown as globules) in a matrix of transformed beta. The hydride aciculae (white in photomicrograph) are readily apparent and are concentrated in the transformed beta; it seems that the hydrides are aligned with and exist in between the transformation products.

The dynamic tensile properties of Zr-2.5Nb were determined prior to delayed failure studies; the results are presented in Table IX and are schematically represented by the curves in Figure 18. The properties of this alloy are very similar to Zr-Al-Sn-Mo except that notch sensitivity is not observed without the presence of hydrogen. In the hydrided condition, however, this material is extremely notch-sensitive and apparently allows for easy crack propagation. (The reduced fracture stress is an average of two specimens, both values being very close to identical.) Thus, for the Zr-2.5Nb alloy, the tensile behavior represents optimum conditions for delayed failure--just as in the case for Zr-Al-Sn-Mo.

The delayed failure study was performed at room temperature on notched specimens containing 500 ppm hydrogen. The results are summarized in Table X, and a curve of these data is shown in Figure 19. The lowest stress at which fracture was observed is only 17,300 psi below the fracture stress, and the shape of the curve indicates that no fractures would occur

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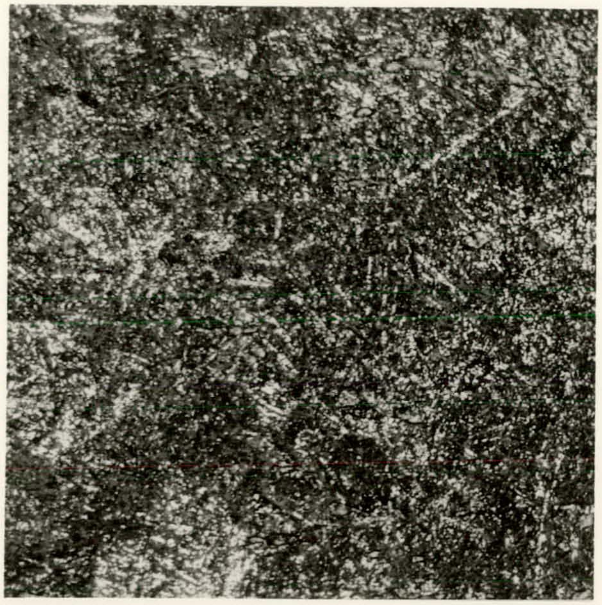

Neg. No. 23727 Mag. X500

Fig. 17

Microstructure of Zr-2.5Nb containing 500 ppm hydrogen. Annealed at 880° C, 30 min ---> WQ; aged 500° C, 7 hours. The white acicular phase is zirconium hydride and seems to be concentrated in the transformed beta (gray). Primary alpha is seen as whitish-gray globules. Anodically etched. (see text for Zr-Al-Sn-Mo).

TABLE IX

DYNAMIC TENSILE PROPERTIES OF Zr-2.5Nb AT ROOM TEMPERATURE

Condition	Ultimate Tensile Strength, psi	Yield Stress, psi (0.2% offset)	Total Elongation, %
Unnotched, vacuum-annealed	129,800	124,000	17.5
Unnotched, 500 ppm H_2	134,000	125,000	18.7
Notched, vacuum-annealed	140,000	--**	(4)*
Notched, 500 ppm H_2	57,300	--**	(2)*

* Values taken from load-extension curve; deformation confined to area around base of the notch.

** Fracture occurred before 0.2 per cent offset or within Hooke's law region of stress-strain curve.

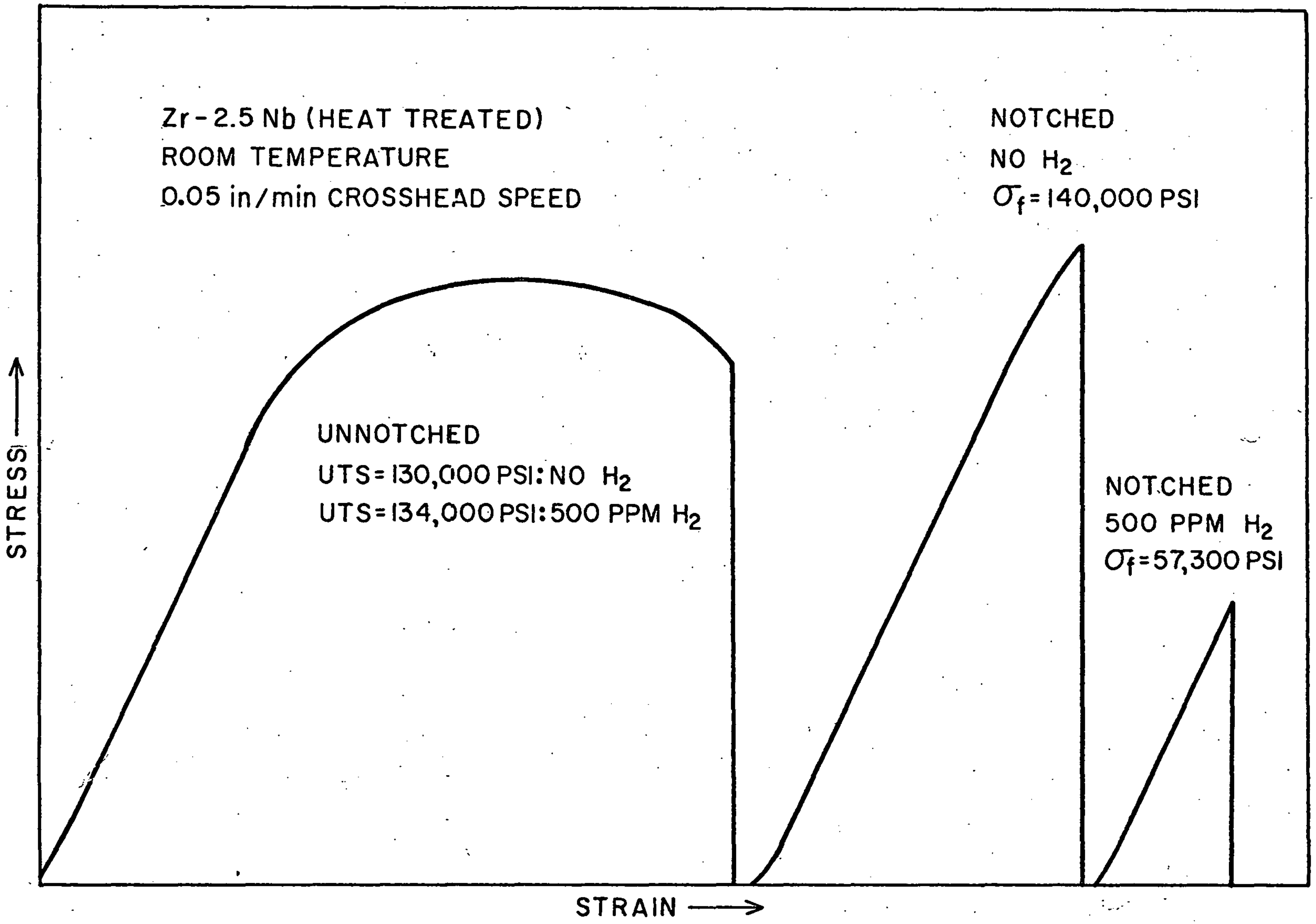

FIG. 18 - SCHEMATIC REPRESENTATION OF DYNAMIC TENSILE PROPERTIES OF Zr-2.5Nb.

TABLE X

SUMMARY OF DELAYED FAILURE EVALUATION OF NOTCHED Zr-2.5Nb SPECIMENS CONTAINING 500 PPM HYDROGEN

Applied Stress, psi	Time to Failure, hr
57,000	< 0.02
55,500	< 0.02
52,000	99.7
47,000	181.7
40,000	222.3
30,000	no failure, 1035 hr
20,000	no failure, 1035 hr

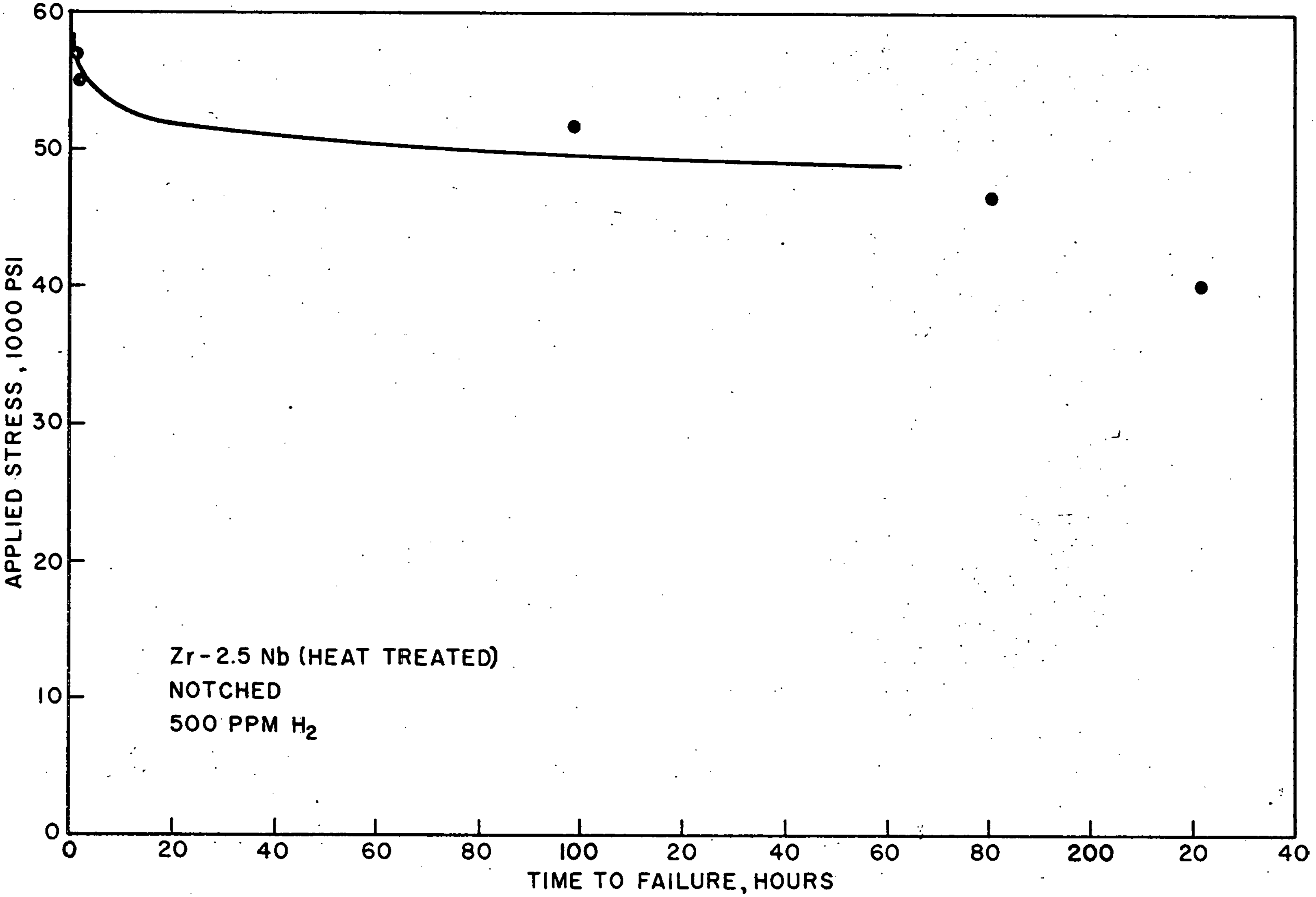

FIG. 19- DELAYED FAILURE EVALUATION OF Zr-2.5Nb ALLOY AT ROOM TEMPERATURE

below this level. The behavior of this material under these conditions is similar to unalloyed zirconium and Zircaloy-2; evidently, at room temperature and with 500 ppm absorbed hydrogen, Zr-2.5Nb is relatively insensitive to static fatigue.

If one uses the stress increment below the fracture stress where time-dependent fracture is observed within 1000 hours as the criterion for delayed failure susceptibility, then Zr-2.5Nb must lie between Zircaloy-2 and Zr-Al-Sn-Mo. Further, if one considers that cracks are nucleated by hydride platelets or the hydrides act as dislocation barriers, then a greater amount of hydride would nucleate more cracks and thereby increase the susceptibility to static fatigue. In order to obtain a cursory verification of these ideas, two specimens of Zr-2.5Nb were hydrogenated to 2000 ppm hydrogen. The materials were heat-treated in the normal manner, notched, and loaded to 45,000 psi and 30,000 psi. Table X shows that similar specimens containing 500 ppm hydrogen should fracture in about 200 hours at 45,000 psi and probably not at all at 30,000 psi. Specimens with 2000 ppm hydrogen fractured in 21.2 hours at the former stress and 51.6 hours at the latter; such results strongly indicate that the susceptibility to delayed failure is greatly increased with high hydrogen contents.

One might extend these results to propose that the delayed failure characteristics of Zr-2.5Nb might vary with hydrogen content in a manner shown in Figure 20. Such behavior again emphasizes the fact that delayed failure of a particular zirconium alloy must be considered in the light of degree or magnitude of sensitivity; it cannot be said that zirconium does not exhibit static fatigue; certain alloys do exhibit this phenomenon to a high degree of susceptibility.

IV. SUMMARY AND CONCLUSIONS

An investigation has been pursued for the purpose of determining the degree of susceptibility of zirconium and zirconium alloys to time-dependent delayed failure as caused by absorbed hydrogen and applied stress. The study and experiments performed in this program lead to the following conclusions.

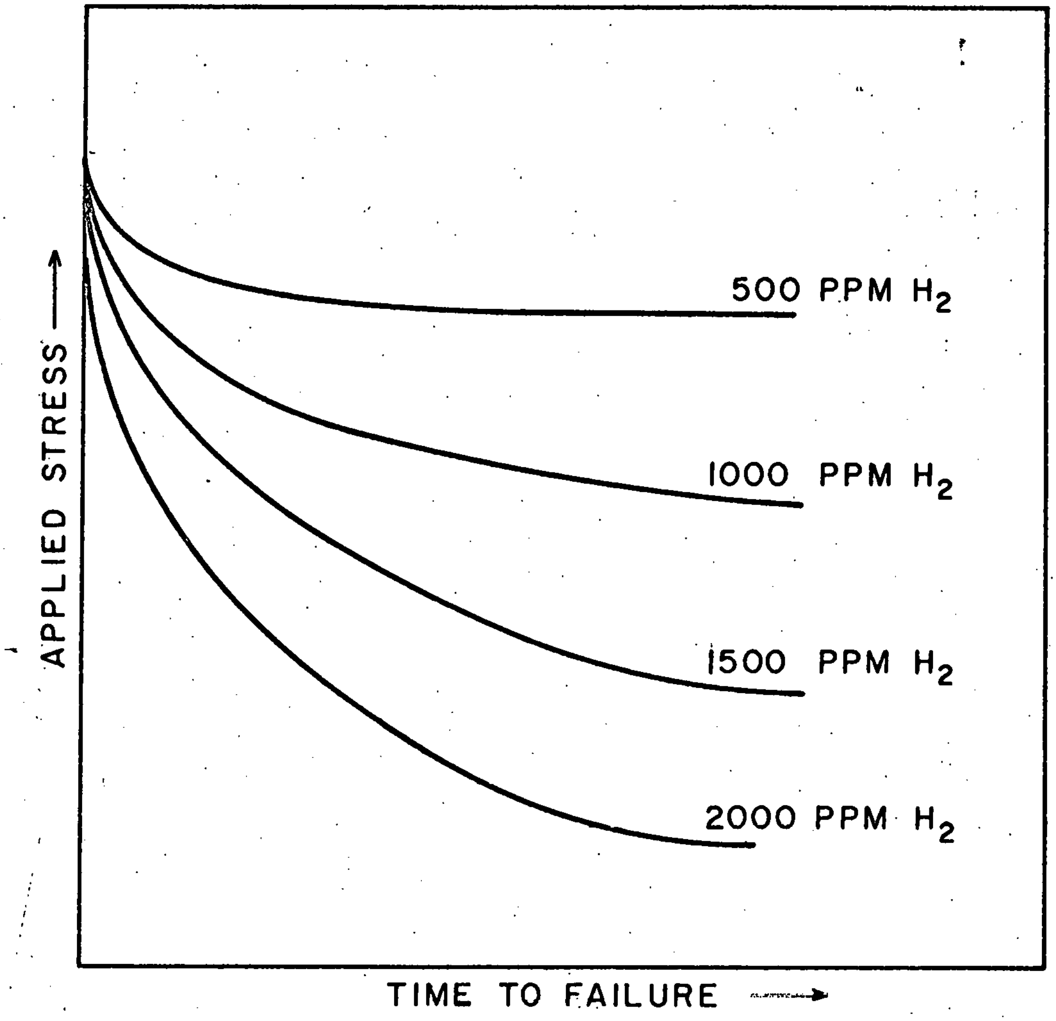

FIG. 20 - SCHEMATIC DELAYED FAILURE CURVE OF Zr-2.5Nb AT ROOM TEMPERATURE WITH 500 ppm HYDROGEN AND POSSIBLE BEHAVIOR AT HIGHER HYDROGEN CONTENTS.

1. Fully annealed, unalloyed zirconium containing 200 ppm or 500 ppm is essentially insensitive to delayed failure at room temperature; the introduction of a notch does not increase the susceptibility to delayed failure.

2. Annealed Zircaloy-2 containing 200 ppm or 500 ppm hydrogen is not markedly susceptible to delayed failure at room temperature; the existence of a notch does not promote delayed failure in this material at these hydrogen levels. Further, extremely coarse-grained material, while reported to cause notch sensitivity in material containing 500 ppm hydrogen, does not cause increased sensitivity to static fatigue. In addition, 20 per cent cold reduction by rolling does not cause increased delayed failure susceptibility of Zircaloy-2 containing 200 ppm hydrogen nor does corrosion and concomitant surface oxidation in 750° F steam. For specimens with 500 ppm hydrogen, quenching to retain a relatively small percentage of hydrogen in solid solution does not promote static fatigue failure.

3. Although Ostberg in Sweden has observed delayed failure in one lot of hydrogen annealed Zircaloy-2 similar to the failure characteristics of hydrogenated titanium, the three different lots of material studied in this program did not exhibit static fatigue at room temperature. No correlation with compositional variations or level of impurities was possible.

4. The alloy Zr-1.25Al-1Sn-1Mo in the notched and unnotched condition containing 500 ppm hydrogen is susceptible to delayed failure at room temperature. At O° C, the susceptibility to static fatigue is apparently intensified; however, at -196° C the sensitivity is diminished. The results obtained strongly indicate that time-dependent fracture due to absorbed hydrogen and applied stress is temperature dependent.

5. The heat-treated alloy Zr-2.5Nb in the notched condition and containing 500 ppm hydrogen is moderately susceptible to delayed failure at room temperature. At a hydrogen level of 2000 ppm, cursory experimental data indicate severe sensitivity of this material to delayed failure; apparently, the occurrence of time-dependent fracture at room temperature is dependent on hydrogen concentration.

V. LOGBOOKS AND CONTRIBUTING PERSONNEL

The data presented in this report are recorded in ARF Logbooks Nos. C-11680, C-11681, C-11682, and C-12216.

Personnel contributing to this work were the following:

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

Respectfully submitted,

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Tech Rev - CRS

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