REPORT CODE SELECTION

Prime Nos IITRI-B6005-11

Secondary Nos. _____
_____

MA

IIT RESEARCH INSTITUTE
formerly Armour Research Foundation of Illinois Institute of Technology

Contract No. AT(11-1)-578
Project Agreement No. 23

RESEARCH DESIGNED TO EVALUATE
Zr-2.5Nb AND Zr-2.5Nb-0.5Cu ALLOYS
FOR DELAYED FAILURE
HYDROGEN EMBRITTLEMENT

IITRI-B6005-11
(Final Report)

Technology Center

Chicago, Illinois 60616

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

IIT RESEARCH INSTITUTE
Technology Center
Chicago 16, ,Illinois

Contract No. AT(11-1)-578
Project Agreement No. 23

RESEARCH DESIGNED TO EVALUATE
Zr-2.5Nb AND Zr-2.5Nb-0.5Cu ALLOYS
FOR DELAYED FAILURE
HYDROGEN EMBRITTLEMENT

D. Weinstein
F. C. Holtz

IITRI-B6005-11
(Final Report)

October 15, 1962 - October 14, 1963

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

November 14, 1963

RESEARCH DESIGNED TO EVALUATE
Zr-2.5Nb AND Zr-2.5Nb-0.5Cu ALLOYS
FOR DELAYED FAILURE
HYDROGEN EMBRITTLEMENT

ABSTRACT

In a previous program, the existence of moderate delayed failure of Zr-2.5Nb with 500 ppm absorbed hydrogen was established. The present investigation is to determine static fatigue susceptibility of this alloy under various conditions of hydrogen content, heat treatment, and metallurgical condition and includes study of the ternary modification Zr-2.5Nb-0.5Cu.

Notched and unnotched specimens were evaluated under static loading conditions, primarily at room temperature and with 500 ppm absorbed hydrogen, and the time to failure and fracture characteristics were determined. The metallurgical history which resulted in significant delayed failure susceptibility consisted of water quenching followed by an aging treatment which gave a matrix of entirely transformed beta. If an alpha-transformed beta microstructure was produced, static fatigue was markedly attenuated. The results can be accounted for by consideration of whether a crack nucleus can propagate through the matrix or be stopped by local plastic yielding. The propagation of cracks is therefore determined by matrix strength and ductility, which appear to be strong factors in determining hydrogen embrittlement.

TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION.	1
II. SCOPE OF INVESTIGATION	5
III. EXPERIMENTAL	6
IV. RESULTS AND DISCUSSION.	7
A. Zr-2.5Nb	10
B. Zr-2.5Nb-0.5Cu	15
C. Microstructural Effect on Delayed Failure of Zr-2.5Nb-0.5Cu	30
D. Effect of a Hydride Surface Layer on Delayed Failure of Zr-2.5Nb-0.5Cu	35
V. CONCLUSIONS	38
VI. LOGBOOKS AND CONTRIBUTING PERSONNEL.	40
REFERENCES	41

LIST OF ILLUSTRATIONS

<u>Fig.</u>		<u>Page</u>
1	Notched Tensile and Delayed Failure Specimen. . . .	8
2	Unnotched Tensile and Delayed Failure Specimen . .	9
3	Static Fracture Behavior at Room Temperature of Zr-2.5Nb: Quenched and Aged, Notched Specimens, 500 ppm Hydrogen.	13
4	Static Fracture Behavior at Room Temperature of Zr-2.5Nb: Quenched and Aged, Unnotched Specimens, 500 ppm Hydrogen.	14
5.	Static Fracture Behavior at Room Temperature of Zr-2.5Nb-0.5Cu: Annealed and Swaged (150° C), Notched Specimens, 500 ppm Hydrogen.	17
6	Static Fracture Behavior at Room Temperature of Zr-2.5Nb-0.5Cu: Quenched and Aged (535° C), Notched Specimens, 500 ppm Hydrogen.	20
7	Static Fracture Behavior at Room Temperature of Zr-2.5Nb-0.5Cu: Quenched and Aged (535° C), Unnotched Specimens, 500 ppm Hydrogen.	21
8	Fracture at Room Temperature of Zr-2.5Nb-0.5Cu Specimens with 500 ppm Absorbed Hydrogen, Statically Loaded at 95 per cent of the Dynamic Yield Stress.	23
9	Area at Fracture of Zr-2.5Nb-0.5Cu with 500 ppm Hydrogen, Showing Crack Initiation at Specimen Surface.	24
10	Crack Propagation in Zr-2.5Nb-0.5Cu Containing 500 ppm Hydrogen Which was Quenched from 825° C and Aged at 535° C for 6 Hours	25
11	Static Fracture Behavior at Room Temperature of Zr-2.5Nb-0.5Cu: Quenched and Aged (400° C), Notched Specimens, 500 ppm Hydrogen	28

<u>Fig.</u>		<u>Page</u>
12	Static Fracture Behavior at Room Temperature of Zr-2.5Nb-0.5Cu: Quenched and Aged (400° C), Unnotched Specimens, 500 ppm Hydrogen.	
13	Crack Propagation in Zr-2.5Nb-0.5Cu Containing 500 ppm Hydrogen Which Was Quenched from 825° C and Aged at 400° C for 6 Hours.	
14	Microstructure of Vacuum-Annealed Zr-2.5Nb-0.5Cu Quenched from 825° C and Aged at 400° C for 6 Hours. . .	
15	Microstructure of Vacuum-Annealed Zr-2.5Nb-0.5Cu Quenched from 825° C and Aged at 535° C for 6 Hours... .	
16	Microstructure of Zr-2.5Nb-0.5Cu Quenched from 825° C and Simultaneously Aged and Hydrided at 535° C for 6 Hours.	
17	Microstructure of Zr-2.5Nb-0.5Cu Quenched from 825° C, Aged at 535° C for 6 Hours, and then Hydrided at 300° C for 6 days	

LIST OF TABLES

	<u>Page</u>
I Dynamic Tensile Properties at Room Temperature of Zr-2.5Nb Annealed 880° C, 1/4 hour--> WQ; Aged 500° C, 24 hours--> AC	12
II Dynamic Tensile Properties at Room Temperature of Zr-2.5Nb-0.5Cu Annealed 825° C, 1/4 hour-->WQ; Aged 535° C, 6 hours--> AC	19
III Dynamic Tensile Properties at Room Temperature of Zr-2.5Nb-0.5Cu Annealed 825° C, 1/4 hour--> WQ; Aged 400° C, 6 hours--> AC.	27

RESEARCH DESIGNED TO EVALUATE
Zr-2.5Nb AND Zr-2.5Nb-0.5Cu ALLOYS
FOR DELAYED FAILURE
HYDROGEN EMBRITTLEMENT

INTRODUCTORY STATEMENT

This is the Final Report of experimental work, covering the period October 15, 1962, to October 14, 1963, on Contract No. AT(11-1)-578, Project Agreement No. 23. This investigation was supported by the USAEC/AECL Collaborative Program, which is administered by the Savannah River Operations Office.

RESEARCH DESIGNED TO EVALUATE
Zr-2.5Nb AND Zr-2.5Nb-0.5Cu ALLOYS
FOR DELAYED FAILURE
HYDROGEN EMBRITTLEMENT

I. INTRODUCTION

Interest in the topic of hydrogen in zirconium stems primarily from the fact that a significant percentage of hydrogen released during corrosion in superheated water or steam finds its way into the metal. The mechanism by which this absorption occurs has not been fully described, and various attempts to completely suppress or markedly attenuate this occlusion have not been entirely successful. That this hydrogen absorption can seriously affect mechanical properties of zirconium is well known. Data are available which clearly show the severe reduction of impact properties due to absorbed hydrogen.⁽¹⁾ Data obtained on zirconium containing various concentrations of hydrogen show marked decreases in tensile ductility and strength.⁽²⁻⁴⁾ Data have recently shown that such material is susceptible to delayed failure.^(5, 6) The present investigation concerns the degree to which Zr-2.5Nb and Zr-2.5Nb-0.5Cu alloys, having various metallurgical histories, are susceptible to delayed failure.

The term "delayed failure" (or static fatigue) can be defined as the fracture of a material due to a combination of absorbed hydrogen, applied stress, and time. This phenomenon has long been known to occur in high-strength steels,^(7, 8) where as little as 2 ppm hydrogen is sometimes sufficient to cause embrittlement, and in certain titanium alloys^(8, 9)--notably those having the alpha/beta microstructure. The definition of delayed failure used above is limited to the case where the active species participating in the fracture process is hydrogen or a hydride. Alternatively, the term "hydrogen embrittlement" could therefore be employed to describe delayed failure as used herein. It must be realized that other

embrittlement phenomena are manifested by delayed failure--such as liquid-metal embrittlement, and stress-corrosion cracking. In recent years, there have been experimental attempts, with some success, to link these three embrittlement processes to the common effect of the active species on surface energy required for crack formation. (10, 11)

To gain knowledge of the importance of hydrogen effects on properties of zirconium, the present state of zirconium technology as applied to cladding and in-core components in superheated water and steam-cooled reactors must be examined. In water to about 360° C, zirconium alloys have been developed which show excellent corrosion resistance and extremely low percentages of hydrogen pickup during corrosion. The strength of these materials is satisfactory for these applications, and there is no particular difficulty in obtaining a zirconium alloy superior to Zircaloy-2 for service in this medium. The status of zirconium alloys for service in steam, however, is quite different. In 400° C steam, for example, zirconium alloys have been developed^(12, 13) which, on the basis of corrosion resistance only, are satisfactory for reactor application. However, by means of alloying additions to zirconium, the amount of hydrogen absorbed during corrosion in this medium has not been reduced to a level acceptable for reactor utilization--particularly as long-time core components. At higher temperatures, the absorption is severely increased and corrosion resistance is unacceptable as well. There has been a great deal of effort⁽¹²⁻¹⁷⁾ directed toward development of zirconium alloys for use in high-temperature steam, but the hydrogen pickup problem has not been solved. At present, therefore, if one desires to use a zirconium alloy in 400° C steam, the effect of hydrogen on mechanical properties of the particular alloy must be known. The uptake of hydrogen during corrosion has become the most important parameter in consideration of zirconium alloy application. In evaluation of properties, besides the effect of hydrogen on impact and dynamic tensile behavior, susceptibility to delayed failure should also be determined.

The suggestion that zirconium alloys might be susceptible to delayed failure as a result of absorbed hydrogen was made over two years ago by Weinstein.⁽¹⁸⁾ Certainly, on the basis of impact and tensile data for hydrided zirconium, an a priori conclusion regarding delayed failure susceptibility could not be made. The proposition was founded on experimental results for the similar element titanium and on theoretical considerations formulated for body-centered cubic metals. At that time, the Petch theory⁽¹⁹⁾ for hydrogen embrittlement of steel, which proposed that hydrogen adsorbed on dislocation crack nuclei reduces surface energy and causes a lowering of fracture stress which then results in brittle fracture, provided at least a cursory theoretical reason why embrittlement might occur in zirconium. (Recently, however, there has been considerable controversy⁽²⁰⁾ on the Petch mechanism.)

An experimental program was initiated to determine whether or not zirconium and its alloys were sensitive to delayed failure. Results⁽⁵⁾ of this investigation showed that unalloyed zirconium and Zircaloy-2 at room temperature containing up to 500 ppm hydrogen were not susceptible to static fatigue fracture. (Almost simultaneously, however, Ostberg⁽⁶⁾ showed contrary evidence that Zircaloy-2 was susceptible to delayed failure.) The high-strength alloy Zr-1.25Al-1Sn-1Mo was evaluated in static tests and exhibited severe delayed failure sensitivity with 500 ppm absorbed hydrogen. Experimental results on notched specimens of Zr-2.5Nb in the quenched and aged condition and containing 500 ppm hydrogen indicated that this material was moderately susceptible to time-dependent, static fracture. Thus, at the outset of the current program, it was established that certain zirconium alloys exhibit the delayed failure phenomenon as a result of hydrogen absorption.

To this juncture, the experimental work was phenomenological only, and no studies were made toward formulation of a fracture mechanism. However, recent work on crack nucleation in hydrided zirconium allowed for a somewhat limited explanation of results.⁽²¹⁾

Studies by Westlake⁽²²⁾ showed conclusively that hydride platelets in zirconium are effective barriers to dislocation motion. Further, he presented evidence showing that the stress at the head of a dislocation pile-up is sufficient to fracture the hydride and thus nucleate a crack in the surrounding zirconium matrix. (Evidence was also given for nucleation of Stroh-type cracks.) In studying a material which was essentially pure zirconium containing hydride aciculae, Westlake found that in no case did a freely propagating crack result from the hydride fracture. In all instances, the application of additional stress caused the crack tip to blunt by local plastic yielding. It follows that propagation of the dislocation-formed crack depends on the properties of the matrix. In turn, delayed failure can occur only if the crack nucleus can grow at the given applied stress--which is a function of the matrix strength. (The instability of microcracks in these materials should be analogous to mathematical attempts to predict whether or not crack propagation occurs in a body-centered cubic metal. A modified Griffith equation relating crack size to strength and effective surface energy is generally employed.) Thus, for unalloyed zirconium and Zircaloy-2 which have matrices of relatively low strength and high ductility, no brittle static fracture resulted. At applied stresses above the yield stress, crack nucleation readily occurred; propagation, however, was arrested by local plastic yielding. For Zr-1.25Al-1Sn-1Mo and Zr-2.5Nb, which have high-strength matrices and exhibit severe notch sensitivity, crack nuclei will readily propagate once they reach a critical size and delayed failure can occur. Obviously, the size of a crack nucleus depends on the magnitude of applied stress. Therefore, the stress below which static fracture does not occur is that where only subcritical size crack nuclei are formed--these being nonpropagating.

The analysis presented above can be compared to recent findings by Klepfer.⁽¹²⁾ In his evaluation of impact properties of experimental alloys containing hydrogen absorbed during steam corrosion, he concludes that acceptable impact resistance for a given hydrogen content is a function of total alloy content. Total alloy content would be generally equivalent to strength of the material. Thus, while a specific alloy might exhibit reasonable impact properties with, say 100 ppm hydrogen, the

same quantity of hydrogen in a higher strength alloy might be intolerable. It is seen that this interrelationship complicates the alloy development effort for steam application. If, by alloying, the amount of hydrogen absorbed during corrosion is markedly reduced, the strength must not be such that even this low hydrogen absorption still results in impact embrittlement. If one considers further the preferred concentration of hydrogen by migration in thermal gradients,⁽²³⁾ the alignment of hydrides perpendicular to tensile stresses,⁽²⁴⁾ and the texture of the material, the tolerance of zirconium alloys for hydrogen becomes quite low.

The Zr-2.5Nb alloy was determined to be susceptible to delayed failure. The investigation carried out during the current year included the study of several variables--heat treatment, cold reduction, hydrogen content, and temperature--on the static fatigue characteristics of both Zr-2.5Nb and Zr-2.5Nb-0.5Cu. It will be seen that the analysis previously presented regarding matrix strength generally holds for these studies. That is, any variable changed such that an increase in strength results, generally will cause increased delayed failure susceptibility.

II. SCOPE OF INVESTIGATION

For Zr-2.5Nb, the condition of heat treatment were the following:

1. Anneal 880° C, 1/4 hr --> furnace cool
2. Anneal 880° C, 1/4 hr --> furnace cool;
cold reduce 30% by swaging.
3. Anneal 880° C, 1/4 hr --> water quench;
age 500° C, 24 hr --> air cool.

For Zr-2.5Nb-0.5Cu, specimens were heat treated as follows:

1. Anneal 825° C, 1/4 hr --> furnace cool.
2. Anneal 825° C, 1/4 hr --> furnace cool;
cold reduce 30% by swaging
3. Anneal 825° C, 1/4 hr --> water quench;
age 535° C, 6 hr --> air cool.
4. Anneal 825° C, 1/4 hr --> water quench;
age 400° C, 6 hr --> air cool.

Specimens in the above heat-treated conditions were to be evaluated in the notched and unnotched condition at room temperature, 250° C, and 300° C; at each temperature and under all other possible combinations, the hydrogen contents to be studied were 500 ppm, 200 ppm, and vacuum annealed. The applied stress was to be constant for all specimens and would be that stress which is 95% of the yield stress (0.2% offset) as determined from dynamic tensile tests. Thus, the minimum number of tensile and delayed failure specimens to be evaluated as outlined above would be 252.

Closer examination of the work scope shows that it is possible to eliminate many conditions without diminishing the value of results or the basis for conclusions. For example, in a given condition of heat treatment and specimen design and at a specific temperature, delayed failure would not be observed with 200 ppm hydrogen if the phenomenon were not observed at the 500 ppm level. Similarly, the absence of static delayed fracture at 250° C indicates that no fracture would be observed at 300° C. On the other hand, delayed failure of notched specimens cannot be determined by a single test. Aside from scatter of data and strength level, the 0.2% offset yield stress does not exist. Generally, one bases delayed failure stress levels on the notched fracture stress, and at least two or three specimens loaded to progressively lower applied stresses are required for even a cursory evaluation of susceptibility. Even then, notched specimens do not allow for examination of crack nucleation, and the results are therefore limited in value. Thus, as will be seen from presentation of data, the number of conditions evaluated was reduced considerably; in certain cases, however, more detailed determinations were carried out.

III. EXPERIMENTAL

The binary and ternary zirconium alloys were obtained* in the form of 1/2-inch diameter rod in the as-fabricated condition. Three-inch long sections were cut from the rods, pickled in the standard HF-HNO₃

---

* This material was supplied by Atomic Energy of Canada, Ltd. Their cooperation in making these alloys available is gratefully acknowledged.

solution, and then hydrogenated in a modified Sieverts apparatus. The details of this equipment and the procedure have been previously described,⁽⁵⁾ hydriding was carried out at 500°C for 24 hours. Heat treatment was performed in sealed, helium-filled Vycor capsules; for quenched specimens, these bulbs were broken in the quenchant, and the specimens were re-encapsulated for aging treatments. Tensile and delayed failure specimens, both notched and unnotched, are machined from these rods to the dimensions shown in Figures 1 and 2. For material which was cold-worked, smaller diameter specimens were prepared, but they were of the same general design. For notched specimens, the radius was further reduced by cutting a 0.001-inch slot in the base. This reduction was accomplished by means of a 0.001 inch diameter, abrasive-coated tungsten wire moving at the notch-base while the specimen rotated. No cold-worked area was observed adjacent to this slot.

Dynamic tensile tests were carried out on a 10,000-lb capacity Instron machine with autographic recording of stress and extension. The crosshead speed was 0.05 in/min (strain rate = 0.036 min^{-1}). Static fatigue evaluation was performed on lever-arm (about 20:1) creep/stress-rupture stands--each one being previously calibrated.

IV. RESULTS AND DISCUSSION

The microstructure of Zr-2.5Nb and Zr-2.5Nb-0.5Cu when quenched from 880°C and 825°C, respectively, followed by aging consists of primary alpha in a matrix of transformed beta. For these compositions, the annealing temperatures are fairly close to the alpha-beta transus. In the case of the ternary alloy, the addition of 200 ppm hydrogen followed by the beta-quench and aging treatment results in only a small amount of alpha remaining in the microstructure. With 500 ppm hydrogen, the microstructure is entirely transformed beta. The hydrogen exists in these alloys primarily as long platelets having somewhat feathery edges and are equally distributed throughout the material. The orientation of these aciculae is random. Conceivably, a small amount of hydrogen could be in solid solution.

MAKE SYMMETRICAL ABOUT ϵ
ALL DIMENSIONS IN INCHES

TOLERANCES $\pm 1/64$ EXCEPT AS NOTED
FINISH: 16 MICRO-INCHES (NOTCH ONLY)

FIG. 1 - NOTCHED TENSILE AND DELAYED FAILURE SPECIMEN

MAKE SYMMETRICAL ABOUT ϵ
ALL DIMENSIONS IN INCHES

TOLERANCES $\pm$ 1/64 EXCEPT AS NOTED
FINISH: 63 MICRO-INCHES EXCEPT AS NOTED

FIG. 2 - UNNOTCHED TENSILE AND DELAYED FAILURE SPECIMEN

A. Zr-2.5Nb

1. 880° C, 1/4 hr --> FC.
880° C, 1/4 hr --> FC, then reduced
30% by swaging (150° C)

Notched and unnotched specimens of the binary alloy in these conditions were evaluated at room temperature and 250° C; the specimens were vacuum-annealed or contained 200 ppm or 500 ppm hydrogen. In dynamic tensile tests, in no case was severe notch sensitivity observed as a result of hydrogen absorption. For specimens at room temperature with 500 ppm hydrogen, the notched tensile fracture stress was only slightly lower than unnotched specimens with or without hydrogen. These results suggest that crack propagation in this alloy when in the annealed or the annealed and cold-worked condition is unfavorable compared to plastic deformation.

Delayed failure susceptibility for these metallurgical conditions was not observed in any case studied. The most severe set of variable--room temperature and 500 ppm hydrogen--did not cause the unnotched specimens to fail within 1000 hours. A notched specimen loaded to 95 per cent of the fracture stress fractured at 170 hours, but an additional specimen stressed at a slightly lower level did not fail in 1000 hours. The fracture of highly stressed notched specimens, as well as unnotched specimens loaded close to the ultimate tensile strength, is due to creep. Evidence supporting this contention is the deformation (necking) of unnotched specimens, and the fact that vacuum-annealed specimens behaved in an identical manner. At 250° C, no failures were observed in unnotched specimens loaded to 95 per cent of the yield stress; notched specimens failed in short times with a matte-like, pseudo fibrous fracture surface--not characteristic of a brittle-type fracture nucleated at the specimen surface. Therefore, from the data obtained at room temperature and 250° C on specimens containing up to 500 ppm hydrogen, Zr-2.5Nb in the annealed or the annealed plus swaged (30 per cent reduction) conditions does not show susceptibility to delayed failure.

2. 880° C, 1/4 hr --> WQ; aged 500° C,
24 hr --> AC

The room-temperature dynamic tensile properties of the binary alloy in the quenched and aged condition are presented in Table I. In the vacuum-annealed condition, no notch sensitivity was observed; this is in agreement with last year's work⁽⁵⁾ on sheet specimens of this material. The material used last year showed an ultimate tensile strength and yield stress about 20,000 psi higher than the present specimens made from rod. Aside from the difference in fabrication procedure, the reduced strength might be accounted for by a lower oxygen content and a threefold increase in aging time. With a hydrogen content of 200 ppm, slight notch sensitivity was obtained; and at the 500 ppm level, more pronounced sensitivity to the notch resulted. However, the degree of notch sensitivity in the present instance is much less than that observed for sheet specimens. The present data show a notched fracture stress 23,000 psi lower than the ultimate tensile strength, whereas sheet material resulted in a difference of 83,000 psi--considerably more severe. This result can be partially explained by the lower strength material used in the current program; the difference in geometry for a given notch radius causes only a small change in the theoretical stress-concentration factor (K_t)--although higher for a sheet specimen.

Investigation of statically loaded notched specimens during last year's program led to the conclusion that Zr-2.5Nb containing 500 ppm hydrogen in the quenched and aged condition was moderately susceptible to delayed failure. Fracture was observed at a stress 17,000 psi below the notched fracture stress in 220 hours of static loading. The static fracture characteristics of material in the present investigation are shown in Figures 3 and 4. It is interesting to note that 97,000 psi was the lowest applied stress where fracture of notched specimens occurred. The time required for this failure was 222 hours, and this applied stress is 21,000 psi below the fracture stress. Thus, comparison with previous results on sheet material would indicate a similar conclusion regarding delayed failure susceptibility. Static fracture behavior of unnotched specimens, as presented in Figure 4, is such that failure is not observed below the yield

TABLE I

DYNAMIC TENSILE PROPERTIES AT ROOM TEMPERATURE
OF Zr-2.5Nb ANNEALED 880° C, 1/4 HOUR --> WQ;
AGED 500° C, 24 HOURS --> AC

Condition	UTS or Fracture Stress, psi	Yield Stress (0.2% offset), psi	Elongation, %
Unnotched, vacuum annealed	109,000	100,000	16.6
Notched, vacuum annealed	222,000	-	-
Unnotched, 200 ppm H ₂	132,000	124,000	10.0
Notched, 200 ppm H ₂	123,000	-	-
Unnotched, 500 ppm H ₂	141,000	132,000	12.2
Notched, 500 ppm H ₂	118,000	-	-

FIG. 3 - STATIC FRACTURE BEHAVIOR AT ROOM TEMPERATURE OF Zr-2.5Nb:
QUENCHED AND AGED, NOTCHED SPECIMENS, 500 PPM HYDROGEN.

FIG. 4 - STATIC FRACTURE BEHAVIOR AT ROOM TEMPERATURE OF Zr-2.5Nb:
QUENCHED AND AGED, UNNOTCHED SPECIMENS, 500 PPM HYDROGEN.

stress. Moreover, it was not possible to observe any surface-nucleated cracks, and in all cases where fracture occurred it was accompanied by some observable plastic deformation. These characteristics would indicate that a creep mode of fracture was operative rather than delayed failure. The data obtained suggest that the susceptibility to static fatigue of the binary alloy is somewhat less than what is indicated by results on notched specimens. In fact, from these data, the unnotched material is apparently not sensitive to delayed failure with 500 ppm absorbed hydrogen.

B. Zr-2.5Nb-0.5Cu

1. 825° C, 1/4 hr --> FC

The fully annealed condition for the ternary alloy showed tensile and delayed failure behavior similar to the binary material in this condition. There was little difference in strength properties of these materials when annealed, and as a result, notch sensitivity of the ternary alloy with 500 ppm hydrogen was not observed.

At room temperature, unnotched specimens loaded at 95 per cent of the yield stress did not fracture in times as long as 1750 hours. In fact, a specimen with 500 ppm hydrogen stressed slightly above the yield stress showed no failure within 1000 hours. For notched specimens under these conditions, fracture was observed in 170 hours at an applied stress of 95 per cent of the fracture stress. Further, a specimen loaded at a stress 20,000 psi below the fracture stress failed in 1490 hours. While fractures were observed in notched specimens, it is questionable whether delayed failure was operative, due to lack of failure in unnotched specimens. Moreover, a matte-like fracture surface was observed which does not indicate freely propagating cracks--in general, a necessary criterion to demonstrate delayed failure susceptibility. Fractures that could be associated with static fatigue were not observed in vacuum-annealed specimens or those containing 200 ppm hydrogen; similarly, specific studies at 250° and 300° C gave no evidence for time-dependent static fracture. Thus, the ternary alloy in the fully annealed condition does not exhibit delayed failure susceptibility with up to 500 ppm hydrogen and at temperatures between room temperature and 300° C.

2. 825°C, 1/4 hr --> FC; reduced 30% by swaging (150°C).

The ternary alloy in the annealed and swaged condition does not exhibit room-temperature notch sensitivity with up to 200 ppm absorbed hydrogen. At the 500 ppm level, however, moderate sensitivity is obtained as manifested by the notched tensile fracture stress being about 17,000 psi lower than the unnotched condition. No notch sensitivity is observed at 250° or 300°C.

Specimens in the unnotched condition and containing 500 ppm hydrogen were statically loaded at room temperature at stresses slightly above the yield stress as well as at 95 per cent of this value. In no case was fracture observed, the time of testing being up to approximately 2300 hours. However, notched specimens under the same conditions showed somewhat surprising fracture behavior as shown in Figure 5. Failure was observed to a stress of 30,000 psi below the notched fracture stress. The magnitude of this stress increment below the fracture stress is somewhat greater than that for conditions where delayed failure is not observed. Nevertheless, this behavior, per se, does not constitute static fatigue susceptibility. First, the fracture surfaces, while somewhat less fibrous or matte-like in appearance than fractured ternary specimens in the annealed condition, are not characteristic of a surface-nucleated crack which propagated in a brittle or semibrittle manner. Second, and most important, unnotched specimens loaded to the vicinity of the yield stress did not fracture. In a notched specimen, unfortunately, it is not possible to make examinations for surface-nucleated cracks. Thus, a more significant evaluation of static fracture behavior would be examination of specimens stressed progressively higher than the yield stress. The fact that moderate notch sensitivity was observed, indicates that somewhat higher stresses than the yield stress are necessary to nucleate a crack of size sufficiently large to be freely propagating. In this way, the mode of fracture nucleation could be determined. While the available data indicate that Zr-2.5Nb-0.5Cu under these conditions is not susceptible to delayed failure, highly stressed unnotched specimens might show contrary results. In any case, delayed failure susceptibility

FIG. 5 - STATIC FRACTURE BEHAVIOR AT ROOM TEMPERATURE OF Zr-2.5Nb-0.5Cu: ANNEALED AND SWAGED (150°C), NOTCHED SPECIMENS, 500 PPM HYDROGEN.

would be comparatively mild. As in the previously reported conditions, there was no indication of static fatigue sensitivity at elevated temperatures.

3. 825°C, 1/4 hr ->WQ; aged 535°C,
6 hr --> AC

The dynamic tensile properties of the ternary alloy in the quenched and aged condition, as it is used in reactor application, are rather good for a water-corrosion resistant zirconium alloy; these properties and the effect of hydrogen and a notch are summarized in Table II. The strength of 117,000 psi in the vacuum-annealed condition along with almost 15% elongation represent highly acceptable properties for zirconium alloys applied to superheated water-cooled reactors. These properties are maintained with 200 ppm hydrogen, and this quantity of interstitial does not result in notch sensitivity. At the 500 ppm level, however, the notched tensile fracture stress is 26,000 psi below the unnotched tensile strength, which signifies considerable notch sensitivity.

Statically loaded specimens containing 500 ppm hydrogen were initially tested at 95 per cent of the notched fracture stress and yield stress. In the former case, fracture occurred almost instantaneously; in the latter, the unnotched specimen fractured at 734 hours of static loading. Additional specimens in this condition were tested in the notched and unnotched condition at different stress levels, and the resulting static fracture curves are shown in Figures 6 and 7. Notched specimens exhibited fairly short times to fracture at stresses about 20,000 psi below the fracture stress. At an applied stress of 55,000 psi, which is 35,000 psi below the fracture stress, failure occurred at 1140 hours of static loading. Unnotched specimens exhibited somewhat less severe fracture characteristics; however, failure was observed at a statically applied stress below the yield stress.

The fracture characteristics shown in Figures 6 and 7 indicate that the quenched and aged condition render Zr-2.5Nb-0.5Cu highly susceptible to delayed failure. The occurrence of fracture, in the absence of macroscopic plastic deformation, at an applied stress below the yield stress of unnotched specimens is strong evidence that the delayed failure

TABLE II

DYNAMIC TENSILE PROPERTIES AT ROOM TEMPERATURE
OF Zr-2.5Nb ANNEALED 880° C, 1/4 HOUR--> WQ;
AGED 535° C, 6 HOURS--> AC

Condition	UTS or Fracture Stress, psi	Yield Stress (0.2% offset), psi	Elongation, %
Unnotched, vacuum annealed	117,000	103,000	14.8
Notched, vacuum annealed	220,000	-	-
Unnotched, 200 ppm H ₂	127,000	116,000	14.2
Notched, 200 ppm H ₂	197,000	-	-
Unnotched, 500 ppm H ₂	116,000	102,000	13.4
Notched, 500 ppm H ₂	90,000	-	-

Note: All notched specimens showed no deviation from linearity
to the stress at fracture.

FIG. 6 - STATIC FRACTURE BEHAVIOR AT ROOM TEMPERATURE OF Zr-2.5Nb-0.5Cu: QUENCHED AND AGED (535°C), NOTCHED SPECIMENS, 500 PPM HYDROGEN.

FIG. 7 - STATIC FRACTURE BEHAVIOR AT ROOM TEMPERATURE OF Zr-2.5Nb-0.5Cu: QUENCHED AND AGED (535°C), UNNOTCHED SPECIMENS, 500 PPM HYDROGEN.

mode of fracture is operative. Identical results are commonly obtained in static fatigue of high-strength steels containing hydrogen. That no necking occurred or that no gross plastic extension was observed can be shown by the macrophotograph in Figure 8. The fracture is normal to the specimen axis, and no "cup-and-cone" was observed which is ordinarily characteristic of a ductile fracture in this material. While plastic deformation is not observed, the fracture surfaces were not completely smooth and, therefore, a purely cleavage fracture did not occur. Nevertheless, these fracture surfaces had a significantly more pronounced crystalline nature than did the fracture surfaces of annealed material.

There is little doubt that crack nucleation of statically loaded specimens in the quenched and aged condition is initiated at the surface. Such behavior is clearly brought out in the macrophotograph in Figure 9. Such evidence further demonstrates that a creep mechanism is not operative in the fracture of this material. Moreover, these cracks are apparently able to propagate through the matrix at specific applied stresses below the yield stress. Figure 10 shows a well-developed crack near the fracture surface of the unnotched specimen loaded at 95 per cent of the yield stress. It is important to note the length of this crack in relation to the sharpness of the crack tip. There is little doubt that this is a propagating crack, for there is no evidence of blunting by local plastic yielding. If local deformation were to occur and cause any significant blunting of the crack tip, the length of this crack would never have reached this present size.

It is interesting to note in Figure 10 that what appears to be a fairly well-developed pore exists near the tip of the crack. Past work in the literature⁽²⁾ has shown that porosity formation in zirconium, near the fracture surfaces, is strain-induced when in the presence of hydrides--either already existing or precipitated during stressing. It is possible that pores are forming ahead of the advancing crack and thereby aiding crack propagation. It might also be possible that strain-induced hydride precipitation occurs ahead of the crack which could also aid propagation.

Neg. No. 24804

Fig. 8

Fracture at room temperature of Zr-2.5Nb-0.5Cu specimens with 500 ppm absorbed hydrogen, statically loaded at 95 per cent of the dynamic yield stress. Note the absence of gross plastic deformation.

Top: 825° C, 1/4 hr--> WQ; aged 535° C, 6 hr--> AC.
Time to fracture = 733.6 hr.

Bottom: 825° C, 1/4 hr--> WQ; aged 400° C, 6 hr--> AC.
Time to fracture = 378.7 hr.

Neg. No. 24807

X17

Fig. 9

Area at fracture of Zr-2.5Nb-0.5Cu with 500 ppm hydrogen showing crack initiation at specimen surface. Quenched (825° C) and aged at 535° C; statically loaded (room temperature) at 95 per cent of dynamic tensile yield stress. Time to fracture = 733.6 hr. Crack initiation (arrows) occurred at specimen surface, ultimately resulting in failure without macroscopic plastic deformation.

Neg. No. 25012

X500

Fig. 10

Crack propagation in Zr-2.5Nb-0.5Cu containing 500 ppm hydrogen which was quenched from 825°C and aged at 535°C for 6 hours. The unnotched specimen was statically loaded at 95 per cent of the yield stress; fracture occurred at 733.6 hours. This surface crack extends for a considerable distance and shows a sharp tip. There is no evidence of crack arrest by plastic yielding or blunting of the crack tip. Note the existence of what appears to be a pore near the crack tip. Matrix is transformed beta plus second-phase precipitate. Etchant: 3HNO₃-2HCl-1HF-14 Glycerin.

Such speculation suggests interesting studies to gain knowledge of crack propagation in hydrided zirconium.

Specimens in this condition of heat treatment and containing 500 ppm hydrogen were evaluated for delayed failure susceptibility at 250° and 300° C. For times up to 1800 hours, no fracture was observed in unnotched specimens loaded at 95 per cent of the yield stress. Vacuum-annealed specimens were evaluated at room temperature and 250° C, and no failures were obtained which could be associated with delayed failure. Similar results were noted for material containing 200 ppm hydrogen. Thus, the 500 ppm hydrogen level and room temperature render Zr-2.5Nb-0.5Cu in the quenched and aged condition susceptible to delayed failure. The effect of hydrogen on the microstructure of this material may be a significant factor in delayed failure sensitivity; additional discussion of this topic will be presented in a later section.

4. 825° C, 1/4 hr --> WQ; aged 400° C,
6 hr --> AC

The dynamic tensile properties of the ternary alloy in the quenched and 400° C aged condition are basically similar to tensile properties of the 535° C aged material. The tensile data for the former aging treatment are summarized in Table III. For unnotched specimens, the yield stress and ultimate tensile strength are higher than for material aged at 535° C; however, the ductility is lowered. It is seen that aging at 400° C also results in a more notch-sensitive alloy. At the 200 ppm hydrogen level, slight tendency for notch sensitivity is obtained. With 500 ppm absorbed hydrogen, the notch sensitivity is very severe--the fracture stress being 50,000 psi lower than the ultimate tensile strength.

The results of delayed failure studies for this condition of heat treatment are similar to data for material aged at 535° C. The static fracture characteristics of the alloy containing 500 ppm hydrogen are presented in Figures 11 and 12. Notched specimens showed fracture in 1400 hours of static testing at an applied stress as low as 39,000 psi below the fracture stress. This stress increment is somewhat greater

TABLE III

DYNAMIC TENSILE PROPERTIES AT ROOM TEMPERATURE
OF Zr-2.5Nb-0.5Cu ANNEALED 825° C, 1/4 HOUR --> WQ;
AGED 535° C, 6 HOURS--> AC

Condition	UTS of Fracture Stress, psi	Yield Stress (0.2% offset), psi	Elongation, %
Unnotched, vacuum annealed	144,000	132,000	12.0
Notched, vacuum annealed	240,000	-	-
Unnotched, 200 ppm H ₂	149,000	135,000	14.4
Notched, 200 ppm H ₂	141,000	-	-
Unnotched, 500 ppm H ₂	139,000	128,000	7.0
Notched, 500 ppm H ₂	88,800	-	-

Note: All notched specimens showed no deviation from linearity to the stress at fracture.

FIG. 11 - STATIC FRACTURE BEHAVIOR AT ROOM TEMPERATURE OF Zr-2.5Nb-0.5Cu: QUENCHED AND AGED (400°C), NOTCHED SPECIMENS, 500 PPM HYDROGEN.

FIG. 12 - STATIC FRACTURE BEHAVIOR AT ROOM TEMPERATURE OF Zr-2.5Nb-0.5Cu: QUENCHED AND AGED (400°C), UNNOTCHED SPECIMENS, 500 PPM HYDROGEN.

than that for 535°C aged specimens and suggests that delayed failure susceptibility is higher in the 400°C aged condition. Evidence that static fatigue sensitivity is increased is provided by comparison of fracture time for unnotched specimens loaded at 95 per cent of the yield stress. The 400°C aged conditions, as shown in Figure 12, results in fracture at 379 hours of static loading, whereas 734 hours were required for fracture at an equivalent applied stress in the 535°C aged alloy. The fractures were perpendicular to the tensile axis, somewhat crystalline in appearance, and occurred without noticeable macroscopic plastic deformation (as shown in Figure 8). Cracks were initiated at the specimen surface, and--as seen in Figure 13--propagation at an applied stress below the yield stress occurred through the matrix; blunting of the crack tip was not observed. There is only slight evidence of porosity formation in advance of the propagating crack. Thus, these data and observations show that the ternary alloy containing 500 ppm hydrogen in the quenched and 400°C aged condition is highly susceptible to delayed failure at room temperature.

At the 200 ppm hydrogen level, delayed failure was not observed at room temperature--even though a slightly notch-sensitive condition existed. At elevated temperatures, no unnotched specimen fractured in any manner which could be associated with the delayed failure phenomenon. A notch-sensitive condition does not exist in the binary or ternary alloy at elevated temperatures, and crack propagation would not, therefore, be favorable.

C. Microstructural Effect on Delayed Failure of Zr-2.5Nb-0.5Cu

The procedure of hydriding the as-received material and then performing a specific heat treatment was followed primarily to allow a long time for hydrogen to distribute evenly throughout the 1/2 inch diameter rod. However, in the case of 500 ppm absorbed hydrogen, the phase equilibrium at 825°C is apparently modified. In Figures 14 and 15 are shown the microstructure of vacuum-annealed Zr-2.5Nb-0.5Cu which was water-quenched from 825°C and aged for 6 hours at 400° and 535°C, respectively. The considerable amount of primary alpha in these microstructures should be noted and compared to the absence of primary alpha

IIT RESEARCH INSTITUTE

Neg. No. 24955

X500

Fig. 13

Crack propagation in Zr-2.5Nb-0.5Cu containing 500 ppm hydrogen which was quenched from 825°C and aged at 400°C for 6 hours. The unnotched specimen was statically loaded at 95 per cent of the yield stress; fracture occurred at 378.7 hours. Crack exhibits a sharp tip with no evidence of arrest by local plastic yielding. Etchant: 3HNO₃-2HCl-1HF-14 Glycerin.

Neg. No. 24954

X500

Fig. 14

Microstructure of vacuum-annealed Zr-2.5Nb-0.5Cu quenched from 825°C and aged at 400°C for 6 hours. Primary alpha (white) in a matrix of transformed beta (gray). Etchant: 1HNO₃-1HF-3 Glycerin.

Neg. No. 25014

X500

Fig. 15

Microstructure of vacuum-annealed Zr-2.5Nb-0.5Cu quenched from 825°C and aged at 535°C for 6 hours. Primary alpha (white) in a matrix of transformed beta containing resolvable aging precipitate. Etchant: 1HNO₃-1HF-3 Glycerin.

in material containing 500 ppm hydrogen (Figures 13 and 10). In reactor application, the material will enter service in the primary alpha-transformed beta condition, and then absorb hydrogen at about 300° C due to water corrosion over a long period of time. Considering the magnitude of time in service as pressure tubes, in-core components, or even fuel cladding, the hydrogen would be homogeneously distributed throughout the material cross section. Obviously, however, an equivalent time could not be devoted to specimen preparation in this program.

Nevertheless, it was possible to duplicate the essential microstructure that would exist in actual reactor operation. Specimens were quenched from 825° C to give the desired starting microstructure, and then aging and hydriding were simultaneously carried out at 535° C for 6 hours in the Sieverts apparatus. The atmosphere during aging contained hydrogen in a quantity such that if absorption were complete, the hydrogen concentration would be 500 ppm. The microstructure resulting from this procedure is shown in Figure 16; primary alpha and transformed beta are clearly seen, and a hydride "network" is obtained which appears to be fairly uniformly distributed. From the increment of pressure drop on the manometer (measuring pressure within the reaction tube), calculations showed that for all specimens at least 450 ppm hydrogen was absorbed within six hours.

The ultimate tensile strength and yield stress of this material were considerably lower than for specimens first hydrided and then heat treated (Table II). These simultaneously aged and hydrogenated specimens had a tensile strength and yield stress of 90, 100 psi and 79, 900 psi, respectively, and an elongation of 23 per cent. A notched specimen had a fracture stress of 140, 000 psi which signifies that the material is not sensitive to notches. Thus, the presence of alpha in the microstructure apparently results in quite different mechanical properties.

The room-temperature static fracture behavior of this material was determined for a notched specimen loaded to 75 per cent of the fracture stress, and for unnotched specimens loaded slightly above and

Neg. No. 25256

X500

Fig. 16

Microstructure of Zr-2.5Nb-0.5Cu quenched from 825°C and simultaneously aged and hydrided at 535°C for 6 hours. Primary alpha (white) in a matrix of transformed beta with a hydride network. Etchant: 3HNO_3 -2HCl-1HF-14 Glycerin.

slightly below the yield stress. In the former case, fracture occurred in 458 hours; however, unnotched specimens did not fracture in 2100 hours of static loading. Compared to previous results on hydrided and heat-treated material with an all transformed beta microstructure, the presence of alpha apparently attenuates delayed failure susceptibility to a significant extent. Considering the ability of each phase to allow crack propagation, these results might be expected. Alpha zirconium, being relatively ductile and of low strength, would favor crack arrest by local deformation at crack tips. Any crack nucleation at the surface would therefore be non-propagating --particularly at applied stresses below the yield stress.

D. Effect of a Hydride Surface Layer on
Delayed Failure of Zr-2.5Nb-0.5Cu

The influence of a brittle surface layer or coating on the mechanical properties of metals is well known. In particular, crack nucleation at the surface is considerably easier, and the ability of the bulk material to plastically deform is very often impaired. In an extreme case, the surface-nucleated crack can propagate through the metal and result in embrittlement.

Hydriding of ternary alloy tensile specimens in the quenched and 535°C aged condition was carried out at 300°C for a period of six days. Both the rate of hydrogen absorption and diffusion in zirconium at this temperature are relatively slow, and the hydride phase was concentrated at the specimen surface--as shown in Figure 17. The pressure change over the six day period indicated that about 490 ppm hydrogen was absorbed (for total amount of specimen). With almost complete conversion to zirconium hydride at the surface, the nucleation of cracks at this area is greatly enhanced. Moreover, highly localized regions exhibited hydride formation to a considerable distance into the specimens. This hydride penetration should allow easy crack propagation.

Neg. No. 25440

X250

Fig. 17

Microstructure of Zr-2.5Nb-0.5Cu quenched from 825°C, aged at 535°C for 6 hours, and then hydrided at 300°C for 6 days. Although the total hydrogen content is about 490 ppm, hydrides are concentrated at the surface. Hydride penetration has occurred in localized areas to form long "stringers" into the material. Etchant: 3HNO₃-2HCl-1HF-14 Glycerin.

The ultimate tensile strength and yield stress of this material at room temperature were 116,000 psi and 106,000 psi, respectively, with 6.6 per cent elongation to fracture. Compared to mechanical properties of this material with 500 ppm hydrogen homogeneously distributed (Table II), an increase in yield stress and a drop in elongation resulted. These changes of properties are due to the constraint imposed on the bulk material by the presence of the hydride surface layer. Note that the ultimate strength has not significantly changed, and the yield stress tends to approach the level of the tensile strength.

Delayed failure susceptibility of this material was determined by statically loading unnotched specimens slightly above, at, and slightly below the yield stress. Fracture was observed only at stresses higher than the yield stress. The times to failure were within one hour after application of load, and some plastic deformation was noted in every instance. Although the hydride "case" exhibited a cleavage fracture, the "core" fracture surface was fibrous. A large number of surface-nucleated cracks were observed in specimens which fractured; however, no cracks were noted in those which did not fail. These results indicate that an applied stress greater than the yield stress is required to nucleate cracks in this material, and when a crack is nucleated, it can easily propagate through the hydride layer but is then arrested by the ductile core material. The short time to fracture is probably due simply to a decrease in cross section after crack nucleation --especially since some cracks are relatively deep due to hydride penetration. It follows, therefore, that surface hydrided Zr-2.5Nb-0.5Cu in the quenched and 535°C aged condition is not susceptible to delayed failure.

It is interesting to consider delayed failure susceptibility of this material if the localized hydride penetration (Figure 17) had extended completely across the specimen diameter. In such a case, it is reasonable to assume that a crack could easily propagate over the entire length and results in fracture without macroscopic plastic deformation. It could be shown, however, that such a morphology is not substantially different than the situation of Louthan and Marshall⁽²⁴⁾ where hydrides are aligned normal

to the specimen axis. Consider a given length of crack nucleus required for instability or propagation through a matrix of a given strength. If hydrides are now aligned with the long axis of platelets perpendicular to the applied stress such that the mean free path between aciculae is less than or of the same magnitude as the critical crack nucleus size, then propagation should occur through the cross section by brittle fracture through the hydride platelets. It is well known⁽²⁴⁾ that such morphologies occur in zirconium as a result of residual or service stresses. The susceptibility of such material to delayed failure has not been determined; however, some cursory data obtained on Zircaloy-2 containing oriented hydrides indicated an extremely marked increase in static fatigue sensitivity. The fracture behavior was entirely different from similar specimens with randomly oriented hydrides; however, the scatter in properties from one specimen to another did not allow for definite conclusions. This variation could easily be overcome, however. For Zr-2.5Nb-0.5Cu or the binary alloy which has a higher strength matrix than Zircaloy-2 and is more notch sensitive, hydrides oriented in the manner described should very strongly influence delayed failure susceptibility.

V. CONCLUSIONS

An investigation was carried out for the purpose of determining the degree of susceptibility to delayed failure of Zr-2.5Nb and Zr-2.5Nb-0.5Cu in various metallurgical conditions. With up to 500 ppm absorbed hydrogen, the binary alloy in the annealed or the annealed and worked condition does not exhibit sensitivity to static fatigue. At the 500 ppm hydrogen level and in the quenched and aged condition, moderate notch sensitivity is induced and notched specimens at room temperature show a propensity for delayed failure. However, unnotched specimens under the same conditions provided results against any severe static brittle fracture susceptibility. The observations that crack nucleation did not occur at the surface and that plastic deformation accompanied fracture represent good evidence against a static fatigue mode of failure.

The ternary alloy containing up to 500 ppm hydrogen and in the annealed condition did not exhibit delayed failure susceptibility.

Swaging this material at 150° C to a 30 per cent reduction in area resulted in a notch-sensitive condition, and specimens with this configuration showed fracture characteristics similar to the binary alloy when quenched and aged. The ternary composition containing 500 ppm hydrogen, quenched from 825° C and aged at 535° or 400° C for 6 hours, is highly susceptible to delayed failure at room temperature. The primary results which support this conclusion are the fracture, without macroscopic plastic deformation, of un-notched specimens at an applied stress below the yield stress and the surface nucleation of cracks at this stress. Moreover, microstructural observation showed no evidence of crack arrest by local plastic yielding at the crack tip. If, however, heat treatment and hydrogenation are carried out by a procedure which produces an alpha-transformed beta matrix, delayed failure susceptibility is significantly reduced. Apparently, alpha zirconium will allow the necessary plastic deformation to occur and cause the crack tip to blunt and become non-propagating. It was further determined that concentration of the hydride phase at the surface of specimens does not result in a higher sensitivity to static fracture. In no case was delayed failure observed at elevated temperatures.

In general, the classical analysis of whether or not a crack nucleus of a given size can propagate through a material offers an explanation of results with fair consistency. By and large, a heat treatment or change in parameters which increased the matrix strength along with decreasing the ductility generally increased delayed failure susceptibility. Perhaps one notable exception to this behavior would be the case where hydride platelets are aligned normal to the tensile axis. Here, fracture could occur through the hydride, and static fracture would then exhibit only a minor dependence on matrix strength.

VI. LOGBOOKS AND CONTRIBUTING PERSONNEL

The data presented in this report are recorded in IITRI Logbooks No. C-13020 and C-13021.

Personnel contributing to this work were the following:

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

Respectfully submitted,

IIT RESEARCH INSTITUTE

D. Weinstein
Research Metallurgist
Metals and Ceramics Research

F. C. Holtz
Senior Metallurgist
Metals and Ceramics Research

DW/rh

Tech Rev - CRS

IIT RESEARCH INSTITUTE

REFERENCES

1. A. P. Young and C. M. Schwartz, "A Fundamental Investigation of Hydrogen Embrittlement in Zirconium," BMI-1100, June, 1956.
2. F. Forsher, "Strain-Induced Porosity and Hydrogen Embrittlement in Zirconium," J. Metals, May, 1956, p. 536.
3. H. H. Burton, "Hydrogen Effects on Zircaloy-2 Tensile Properties," HW-61077, July 1959.
4. R. L. Mehan and F. W. Weisinger, "Mechanical Properties of Zircaloy-2," KAPL-2110, February, 1961.
5. D. Weinstein and F. C. Holtz, "Delayed Failure Hydrogen Embrittlement of Zirconium," ARF-2230-12, October, 1962.
6. G. Ostberg, Aktiebolaget Atomenergi, Stockholm, Sweden, unpublished work communicated to D. Weinstein, 1962.
7. R. P. Frohberg, W. J. Barnett, and A. R. Troiano, "Delayed Failure and Hydrogen Embrittlement in Steel," Trans. ASM, Vol. 47, 1955, p. 892.
8. A. R. Troiano et. al., "Hydrogen Embrittlement in Steels, Titanium Alloys, and Several Face-Centered Cubic Alloys," WADD TR 59-172, April, 1959.
9. A. E. Riesen and D. H. Kah, "Hydrogen Embrittlement of Titanium Alloys," WADD TR 60-275, October, 1960.
10. E. G. Coleman, D. Weinstein, and W. Rostoker, "On A Surface Energy Mechanism For Stress-Corrosion Cracking," Acta Met., Vol. 9, 1961, p. 491.
11. H. Nichols and W. Rostoker, "Analogies Between Stress-Corrosion Cracking and Embrittlement by Liquid Metals," ASM Trans. Quarterly, Sept. 1963, p. 494.
12. H. H. Klepfer, "Specific Zirconium Alloy Design Program," GEAP-4211 (April, 1963) and GEAP-4284 (July, 1963).
13. D. Weinstein and F. C. Holtz, "Improved Zirconium Alloys," IITRI-B198-46, September, 1963.

14. J. P. Pemsler, "Corrosion of Zirconium Alloys in 900 and 1000° F Steam," NMI-1235, March, 1960.
15. S. Greenberg and C. A. Youngdahl, "Zirconium Alloys for Superheated Steam," to be published.
16. B. Cox, M. J. Davies, and A. D. Dent, "The Oxidation and Corrosion of Zr and Its Alloys: X. Hydrogen Absorption During Oxidation in Steam and Aqueous Solutions," AERE-M621, April, 1960.
17. B. Cox, Ibid. "XII Hydrogen Absorption by Zircaloy-2 and Some Other Alloys During Corrosion in Steam," AERE-R3556, January, 1961.
18. D. Weinstein, Zirconium Meeting, Savannah River Operations, March, 1961.
19. N. J. Petch, "The Lowering of Fracture Stress due to Surface Adsorption," Phil. Mag., Vol. 1, 1956, p. 331.
20. B. A. Bilby and J. Hewitt, "Hydrogen in Steel--the Stability of Microcracks," Acta Met., Vol. 10, 1962, p. 594.
21. D. Weinstein and F. C. Holtz, "Susceptibility of Zirconium and Zirconium Alloys to Delayed Failure Hydrogen Embrittlement," submitted to ASM.
22. D. G. Westlake, "Initiation and Propagation of Microcracks in Crystals of Zirconium-Hydrogen Alloys, ASM Trans. Quarterly, Vol. 56, 1963, p. 1.
23. J. M. Markowitz, "Hydrogen Redistribution in Zircaloy-2 Under Thermal and Mechanical Stress Gradients," WAPD-TM-171, January, 1959.
24. M. R. Louthan and R. P. Marshall, "Tensile Properties of Zircaloy With Oriented Hydrides," Proceedings USAEC Symposium on Zirconium Alloy Development, GEAP-4089, November, 1962.