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RESEARCH DESIGNED TO EVALUATE Zr-2.5Nb AND Zr-2.5Nb-0.5Cu ALLOYS FOR DELAYED FAILURE HYDRIDE SUSCEPTIBILITY

Contract No. AT(11-1)-578

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

Technology Center Chicago 16, Illinois

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April 15, 1963 - July 14, 1963
Contract No. AT(11-1)-578
Project Agreement No. 23

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July 8, 1963

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ABSTRACT

A program is in progress to determine the extent to which Zr-2.5Nb and Zr-2.5Nb-0.5Cu exhibit delayed failure under various conditions of hydrogen content, heat treatment, ambient temperature, and specimen geometry. Specimens are hydrogenated to 200 ppm or 500 ppm in a modified Sieverts apparatus, heat treated or cold reduced (150° C), and then evaluated in dynamic tensile and delayed failure tests.

Data presented on the ternary alloy show that the beta-quenched and aged condition promotes a high sensitivity to static fatigue fracture. At room temperature, unnotched specimens containing 500 ppm hydrogen showed ordinary dynamic tensile stress-strain properties with very good values of strength and elongation. However, at an applied stress of 95 per cent of the yield stress, static fracture--in the absence of macroscopic plastic deformation--occurred after several hundred hours. Photomicrographs are presented showing the brittle crack propagation through the microstructure; mechanisms for such behavior are still speculative, however.

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I. INTRODUCTION

This is the third Quarterly Report covering the period April 15 to July 14, 1963, on Contract No. AT(11-1)-578, Project Agreement No. 23. This investigation is being conducted under the auspicies of the USAEC/AECL Collaborative Program.

Delayed failure (or static fatigue) is the term applied to the static fracture of a material due to the combined effects of absorbed hydrogen, applied stress, and time. This phenomenon has long been known to occur in high-strength steels, and static fatigue has been observed in titanium alloys for almost a decade. The presence of hydrogen in zirconium is known to cause impact embrittlement and loss in tensile ductility (at ordinary strain-rates). Only recently, however, has it been shown that zirconium alloys containing hydrogen are also susceptible to delayed failure. Investigations performed last year under the Collaborative Program showed that a high-strength zirconium alloy with 500 ppm hydrogen was highly susceptible to delayed failure at room temperature. In Sweden, Ostberg communicated that Zircaloy-2 was sensitive to static fatigue under certain conditions. At present, there is no doubt as to the existence of delayed failure in certain hydrided zirconium alloys.

The present program, which is a ramification of last year's investigation, is for evaluation of delayed failure susceptibility of Zr-2.5Nb and Zr-2.5Nb-0.5Cu alloys under various conditions of hydrogen content, heat treatment, temperature, and metallurgical history. It was shown that the binary alloy containing 500 ppm hydrogen was moderately susceptible to static fracture, and this sensitivity was more pronounced at a higher hydrogen content. Since this alloy or the copper-modified composition will be used in the Canadian heavy-water moderated power reactor as pressure tubes and other in-core components, it is important that the delayed failure characteristics of these materials be described.

II. EXPERIMENTAL

The apparatus used in this program, the specimen design, and the experimental procedures have been previously outlined; only a brief discussion of certain procedures and of work scope will be given here. A detailed description of experimental techniques will be given in the final report.

The scope of work for the current year includes study of Zr-2.5Nb and Zr-2.5Nb-0.5Cu having three different metallurgical histories: fully annealed, annealed and cold worked, and beta-quenched and tempered. Delayed failure evaluation is performed at room temperature, 250° C, and 300° C; specimens (notched and unnotched) are vacuum annealed or contain 200 ppm or 500 ppm hydrogen. The applied stress is 95 per cent of the dynamic tensile yield stress or notched fracture stress.

Tensile and static fatigue specimens have been prepared by first hydrogenating in a modified Sieverts apparatus at 500° C for 24 hours. Following this operation, the appropriate heat treatment is performed which, in the case of Zr-2.5Nb-0.5Cu, starts with an 825° C anneal. One should note that this procedure does not closely reproduce the manner in which hydrogen would be absorbed during actual reactor operation. As will be discussed later, the stage during the heat treatment at which hydrogen is introduced may be significantly affecting delayed failure susceptibility.

III. RESULTS AND DISCUSSION

In the last Quarterly Report (ARF-B6005-5), tabulated data were presented on the ternary alloys for specific conditions of heat treatment, temperature, hydrogen content, and specimen geometry. Since that time, the amount of data has grown considerably, and to present all numerical data--at this time--would serve little purpose. It would be more expedient, on the other hand, to simply discuss results under the heading of a specific metallurgical history and use actual data only when necessary. Thus, the detailed presentation of all numerical data will be deferred to the final report.

A. Zr-2.5Nb-0.5Cu: 825°C, 1/4 hr --> Furnace Cool

For this heat treatment, all room-temperature static fatigue tests have been completed. That is, both notched and unnotched specimens, vacuum annealed or with 200 ppm and 500 ppm hydrogen, have been evaluated. In addition, specimens in the notched and unnotched condition containing 500 ppm hydrogen have been statically tested at 250° and 300° C. In no instance have the data indicated that the ternary alloy is susceptible to delayed failure in this condition. For example, unnotched specimens with 500 ppm hydrogen have been statically stressed at 95 per cent of the yield stress for over 1700 hours without signs of surface cracking or fracture. When a notch is introduced, the dynamic tensile curve shows straight line behavior to the fracture stress. Calculation of a yield stress is meaningless, and the total elongation is also without significance. Specimens which are subsequently loaded to 95 per cent of the notched fracture stress have, with only one exception, exhibited fracture in a very short time--generally, immediately after load application. Now if one desires to accurately determine whether or not a notch induces delayed failure in an otherwise insensitive material, a complete set of data points, for stresses considerably lower than the notched fracture stress, is necessary. The fractures observed shortly after loading the notched specimens are due to variation of fracture stress from one specimen to another as well as creep (the third stage of creep is rapidly reached at these high levels of applied stress).

The rapid fracture of notched specimens at high applied stress does not necessarily indicate delayed failure susceptibility. Unless fracture is observed in unnotched specimens at stresses in the vicinity of the yield stress, the material is not susceptible to delayed failure. It is our contention that the latter condition must be satisfied for an affirmative conclusion to result. This requisite follows from the fact that delayed fracture susceptibility is a physical characteristic of the material, the microstructure, and such other parameters which are independent of specimen geometry. In addition, in all known cases of materials sensitive to delayed failure, including the high-strength zirconium alloy previously studied, fracture is observed at stresses below the yield stress. The notch, however, will act to change the magnitude of stresses over which failure will be observed in an already susceptible material.

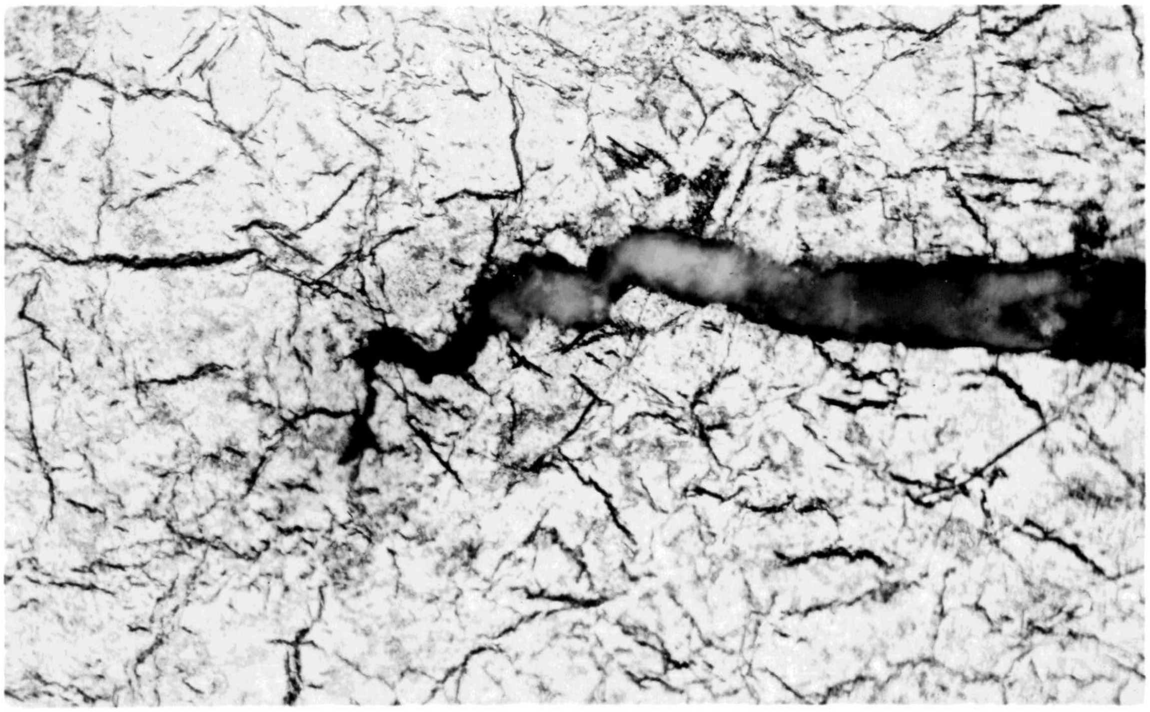
B. Zr-2.5Nb-0.5Cu: 825° C, 1/4 hr--> Furnace Cool; Reduce 30% by Swaging at 150° C

Results of delayed failure evaluation are available for this metallurgical condition at room temperature for all hydrogen contents and for specimens containing 500 ppm hydrogen at 250° and 300° C. There are no results which show conclusively that material in this condition is susceptible to delayed failure. However, there does seem to be a somewhat increased sensitivity to static fracture which will require additional work for verification. For example, a notched specimen at room temperature with 500 ppm hydrogen failed in 8 hours at 95 per cent of the fracture stress. At an applied stress of 75 per cent of the notched fracture stress, a similar specimen failed in 330 hours. On the other hand, an unnotched specimen loaded at 95 per cent of the yield stress did not fail during a test time of about 2200 hours. At the 200 ppm hydrogen level, similar results were obtained on notched and unnotched specimens. Thus, a few notched specimens with 500 ppm hydrogen will be evaluated at progressively lower stresses, and an unnotched specimen will be tested at or slightly above the yield stress. At elevated temperatures, no fractures were observed which could be associated with the delayed failure phenomenon.

C. Zr-2.5Nb-0.5Cu: 825° C, 1/4 hr--> Water Quench; Age 535° C, 6 hr--> Air Cool

A similar, relatively complete set of data is available on the ternary alloy in the quenched and 535° C aged condition. In this condition, the strength of the alloy is markedly increased while maintaining usable ductility. As in the other cases, the introduction of hydrogen and a notch results in "notch sensitivity" for this condition, however, the sensitivity is quite severe. It should be pointed out that the quenched and aged condition imparts the required superheated water corrosion resistance to this alloy which makes it useful in pressure tube applications. However, as detailed in the previous Quarterly Report, this heat treatment also results in a high susceptibility to delayed failure. An unnotched specimen with 500 ppm hydrogen loaded below the tensile yield stress fractures, without evidence of plastic deformation, in 733.6 hours of test at room temperature. Photographs (previously presented) of the specimen surface in the vicinity of fracture showed a number of surface-nucleated cracks normal to the specimen axis. (A ductile tensile fracture would be nucleated at the center of the specimen.) At elevated temperatures, no fractures associated with delayed failure have been observed.

Metallographic observation of cracks was carried out with the hope that such studies might shed light on the fracture mechanism involved in static fatigue. Figure 1 shows a well-developed crack near the fracture surface of material containing 500 ppm hydrogen. Note first the absence of any pro-monotectoid alpha zirconium; at 825° C, it is obvious that the hydrogen additions resulted in an all-beta microstructure which transforms on quenching. On aging at 535° C for 6 hours, a fine, second-phase precipitate is formed as well as hydride aciculae. It is important to note the length of this crack in relation to the sharpness of the crack tip. Little doubt remains that this is a propagating crack and does not show evidence of blunting by local plastic yielding. Moreover, it appears that the crack path follows hydride platelets. Yet, it is not at all certain that these particular hydrides were present in the microstructure prior to crack initiation and propagation. Evidence that such stress- or strain-induced hydride precipitation might be occurring is provided by the well developed pore near the crack tip. Past work in the literature has shown that porosity formation in zirconium, near the fracture surface, is strain-induced when in the presence of hydride--either already existing or precipitated during stressing. It is possible that these pores are at least aiding crack nucleation and propagation.



Neg. No. 25012 Mag. X500

Fig. 1

Microstructure of Zr-2.5Nb-0.5Cu containing 500 ppm hydrogen quenched from 825°C and aged at 535°C for 6 hours. The unnotched specimen was statically loaded at 95% of the yield stress; fracture occurred at 733.6 hours. Surface crack extending for a considerable distance shows a sharp tip which appears to propagate along hydride platelets. Matrix is transformed beta plus second phase precipitate.

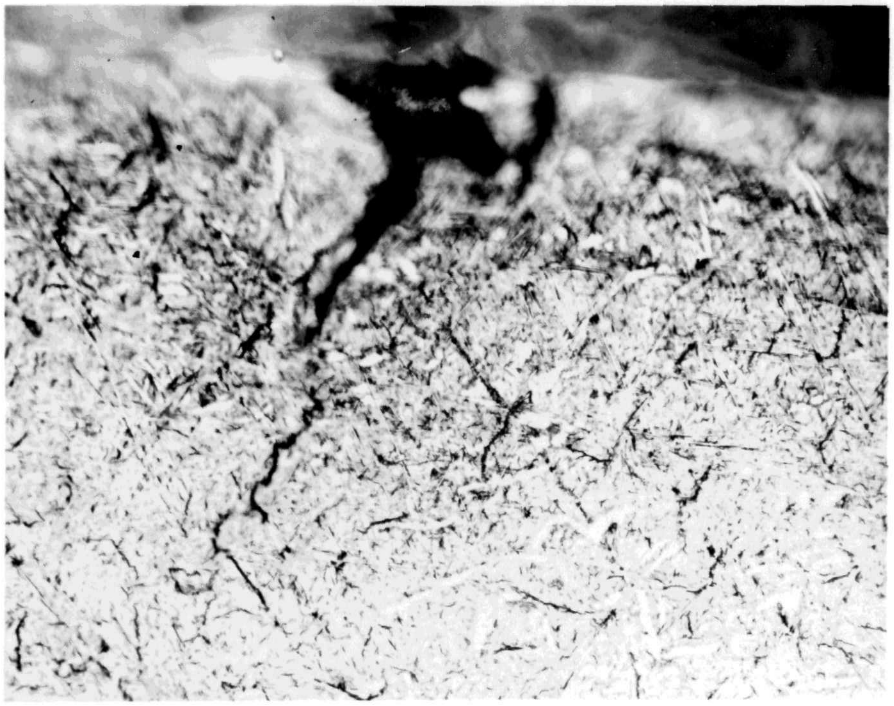
Etchant: $3HNO_3$:2HCl:1HF:14 Glycerin.

The mechanism of static fatigue of hydrided zirconium is highly speculative. Indeed, no strain-induced precipitation is at all necessary if the dislocation-hydride platelet interaction is considered. Crack nucleation by this method has been documented by Westlake at Argonne National Laboratory. Further, it is interesting to note that as the strength level of the material increases, the tendency to delayed failure is also increased. (Discussion to be presented on material aged at 400° C, which is of higher strength than 535° C aged material, shows an even greater susceptibility to delayed failure. Moreover, the Zr-Al-Sn-Mo alloy covered last year is even higher in strength and extremely susceptible to static fracture. The analogy can be carried to steels and titanium alloys as well.) This behavior is related to the properties of the matrix and the ease with which a crack can propagate through it or, roughly, its notch sensitivity. Until more basic studies on fracture of hydrided zirconium can be performed, embrittlement mechanisms will remain speculative.

D. Zr-2.5Nb-0.5Cu: 825° C, 1/4 hr--> Water Quench; Age 400° C, 6 hr--> Air Cool

An unnotched specimen of this material containing 500 ppm hydrogen showed static fatigue (room temperature) at 378.7 hours of testing. The applied stress was 95 per cent of the tensile yield stress. In work on notched specimens, fracture has occurred in 486.5 hours in a specimen loaded to 65 per cent of the notched fracture stress. This material is highly susceptible to delayed failure at room temperature; however, no data for this condition indicate static fatigue sensitivity at 250° or 300° C.

The microstructure and crack formation of material quenched from 825° C and aged at 400° C is shown in Figure 2; the hydrogen content is 500 ppm. Hydrides are shown as black aciculae, and it seems that a considerable amount of alpha has formed during the aging treatment. The crack tip is very sharp and without evidence of blunting by local plastic deformation. It is difficult to determine whether or not the crack propagates along hydride platelets; in this micrograph, the crack appears transgranular and does not seem to follow any specific grain boundary or group of hydride platelets.



Neg. No. 24955 Mag. X500

Fig. 2

Microstructure of Zr-2.5Nb-0.5Cu containing 500 ppm hydrogen quenched from 825°C and aged at 400°C for 6 hours. Photograph shows surface crack near the fracture of statically loaded specimen. Note the sharp crack tip and the apparent transgranular propagation.

Etchant: $3HNO_3$:2HCl:1HF:14 Glycerin.

IV. FUTURE WORK

The investigations to be performed, up to the end of the current year fall under three general topics. First, data on the binary alloy in static fatigue tests will be obtained. A large number of these specimens are presently being prepared and, for some conditions, data are already available. A detailed analysis of results will be presented in the Summary Report. Second, work will be performed on the ternary alloy to fill in certain gaps in the data. The purpose in doing this will be to allow more definite conclusions to be made on failure susceptibility. Third, static fatigue studies will be carried out on material which is already heat-treated prior to hydrogenation. Hopefully, the microstructural change might reduce the fracture tendency of quenched and aged material. In all instances, metallographic observation will supplement the experimental results.

V. CONCLUSIONS

The ternary alloy Zr-2.5Nb-0.5Cu has been evaluated for delayed failure susceptibility under certain conditions of heat treatment, temperature, hydrogen content, and specimen geometry. In the annealed condition, unnotched specimens are not sensitive to delayed failure with up to 500 ppm hydrogen; more data are necessary to confirm the same conclusion for notched specimens. Specimens (500 ppm hydrogen) which were annealed, swaged (30 per cent reduction at 150° C), and notched showed room-temperature failure in 330 hours at an applied stress of 75 per cent of the fracture stress. In the beta-quenched and aged conditions, the sensitivity to delayed failure is markedly increased. Fracture is observed in unnotched specimens statically loaded to 95 per cent of the yield stress (room temperature, 500 ppm hydrogen). Thus, while this heat treatment yields the best dynamic mechanical properties (and the required corrosion resistance), it is perhaps the least desirable from the standpoint of delayed failure. As yet, data available on the binary Zr-2.5Nb alloy are not sufficient to allow meaningful conclusions.

VI. LOGBOOKS AND CONTRIBUTING PERSONNEL

The information contained in this report is recorded in IITRI Logbooks No. C-13020 and C-13021.

Personnel contributing to this work are the following:

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

Respectfully submitted,

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