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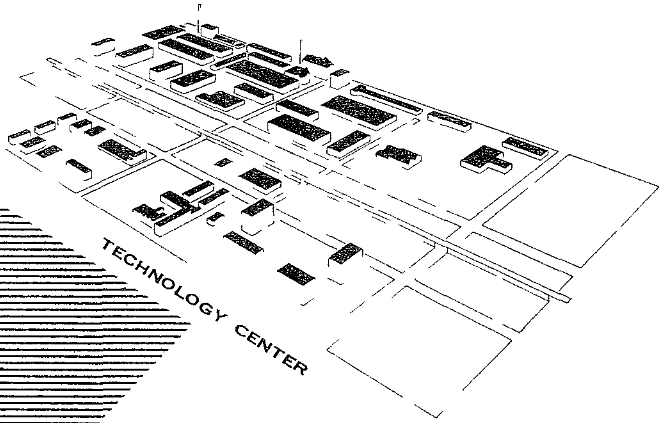
ARF 2230-6
(Quarterly Report No. 2)

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY



DELAYED FAILURE HYDROGEN EMBRITTLEMENT OF ZIRCONIUM

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

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

Attention: Mr. Fred C. Mattmueller
Director
Contracts Division

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

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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. Both notched and unnotched specimens of unalloyed zirconium and Zircaloy-2 have been hydrogenated to 200 ppm and 500 ppm by means of a modified Sieverts apparatus; specimens were evaluated at room temperature.

Thus far, no time-dependent fracture has been observed which can be attributed to the delayed failure phenomenon; it appears that these materials are relatively insensitive to static fatigue. The effects of grain size, temperature, cold deformation, and superheated water and steam corrosion on susceptibility to delayed failure are being determined.

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I. INTRODUCTION

This is the second Quarterly Report, covering the period December 15, 1961, to March 14, 1962, on Contract No. AT(11-1)-578, Project Agreement No. 14. This investigation is being conducted under the auspices of the USAEC/AECL Collaborative Program.

For the assembly or construction of various structures or systems, very often the long-time mechanical properties of the materials represent a primary design criterion. In the pressurized water reactor, zirconium alloys are employed as in-core structural elements, pressure tubes, and other stress-bearing components; a service lifetime of approximately 20 years is desired for these components which is based mainly on the corrosion rate in superheated water. Creep and stress-rupture properties of Zircaloy at elevated temperatures have been studied; however, the time-dependent phenomenon of delayed failure (static fatigue) as caused by the presence of hydrogen has received little attention.

It was recognized several years ago that zirconium absorbs hydrogen during corrosion in superheated water and steam. Shortly after this, the loss of impact properties after exposure to these media was attributed to the presence of zirconium hydride as a grain boundary and matrix (to a lesser extent) platelet phase, and extensive investigation of this phenomenon has followed. Unfortunately, such an approach has resulted in an almost complete neglect of perhaps an equally important manifestation of hydrogen occlusion--the delayed failure phenomenon. Thus, the purpose of the present investigation is to determine the extent to which zirconium exhibits delayed failure as caused by a combination of absorbed hydrogen and applied stress.

One does not know, a priori, that zirconium does not exhibit delayed failure. While this phenomenon is usually associated with high-strength steels and other body-centered cubic metals, delayed failure has been observed in titanium alloys and some face-centered cubic alloys. Moreover, current theories for hydrogen embrittlement do not preclude the possibility of static fatigue occurring in zirconium. In fact, considering the amount of corrosion hydrogen pickup during reactor service and the possibility of subsequent localized concentration due to migration in thermal and mechanical stress gradients--as well as the utilization of higher strength alloys--one might anticipate some susceptibility to delayed failure.

II. MATERIALS, APPARATUS, AND PROCEDURES

Delayed failure studies are being carried out initially on notched and unnotched specimens of unalloyed zirconium and Zircaloy-2. Hydrogen is introduced by means of a modified Sieverts apparatus, and initial evaluation of delayed failure susceptibility is carried out at room temperature. A more detailed description of materials, specimen design, apparatus, and experimental procedures has been presented in Quarterly Report No. 1 (ARF 2230-3).

The method of producing a 0.001 inch notch radius has been modified. Previously, an extremely sharp wedge was pressed into the as-machined notch which caused local upsetting and subsequent recrystallization during hydrogenation in the Sieverts apparatus. The method presently being used employs 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 approximately 0.003 inch. No recrystallization is observed after hydrogenation of such a specimen, and the notch radius is somewhat less than 0.001 inch.

III. RESULTS AND DISCUSSION

The investigation of delayed failure of zirconium and Zircaloy-2 has rapidly proceeded since the last Quarterly Report. The paragraphs to follow describe these studies and present conclusions obtained from experimental results.

The program was initiated on unalloyed zirconium and Zircaloy-2 in the notched and unnotched condition. Specimens contained 200 ppm hydrogen primarily as a grain boundary, acicular hydride precipitate, and delayed failure tests were carried out at room temperature; the materials were in the fully annealed condition and had a uniform, fine grain size. After the dynamic tensile properties were determined, specimens were loaded at stress levels ranging from just below the ultimate stress to below the yield stress. None of the specimens of unalloyed zirconium or Zircaloy-2 exhibited delayed failure over the arbitrarily chosen time limit of 1000 hours. Although some fractures were observed, they occurred at stresses near the ultimate tensile strength and were probably due to creep or actual loading beyond the ultimate. These studies lead to the conclusion that fine-grained, annealed, unalloyed zirconium and Zircaloy-2 containing 200 ppm hydrogen as a grain-boundary precipitate are not susceptible to delayed failure.

At this juncture, the level of hydrogen content was increased to 500 ppm and only notched specimens of zirconium and Zircaloy-2 were prepared for static fatigue. Dynamic tensile tests resulted in slightly lower ultimate strengths and elongations with 500 ppm hydrogen as compared with specimens containing 200 ppm hydrogen showing that there is a slight tendency for increased notch sensitivity with increased hydrogen content. (For unnotched Zircaloy-2, the tensile strength increased and the ductility decreased with greater amounts of hydrogen. These results are in agreement with the more extensive investigation of hydrogen effects on tensile properties by Burton.[1] For unnotched, unalloyed zirconium, the tensile strength remains relatively constant with hydrogen contents up to 500 ppm; the elongation, however, significantly decreases.) Delayed failure evaluation was carried out at room temperature with applied stresses ranging from just below the ultimate stress to the yield stress. Similar results have been obtained at the 500 ppm level in that no fractures could be definitely attributed to the static fatigue phenomenon.

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(1) H. H. Burton, "Hydrogen Effects on Zircaloy-2 Tensile Properties," HW-61077, July 10, 1959.

Graphically, the behavior of static fatigue tests on zirconium and Zircaloy-2 is represented schematically by curve A in Figure 1. Obviously, the characteristics of this curve are unlike those of curves B and C which represent, respectively, delayed failure of a titanium alloy and a high-strength steel. From the fact that fracture occurs only at very high stresses and the fact that no fractures are observed (to 1000 hours) at applied stresses about 10,000 to 15,000 psi below the ultimate, one concludes that zirconium and Zircaloy-2 are relatively insensitive to delayed failure due to hydrogen absorption.

Recent data in the literature[2] suggested that coarse-grained Zircaloy-2 might exhibit a greater susceptibility to delayed failure due to the extreme notch sensitivity of such a material when containing 500 ppm hydrogen. An extremely large grain size was produced by tensile straining a 1-inch wide sheet seven per cent (3-inch gage length) followed by a recrystallization anneal at 800°C for 65 hours. The resulting large grain size is shown in the photomicrograph of Figure 2, which may be compared to an unstrained material given an identical anneal, Figure 3. Critical straining was carried out by tension rather than rolling in hopes that the more uniform deformation would result in a more uniform grain size than that normally obtained in worked and recrystallized Zircaloy. The microstructure of Figure 2 is only slightly larger in grain size, and has about the same uniformity as obtained using the phenomenon of secondary recrystallization recently reported by Reed-Hill.[3] Dynamic tensile tests of unnotched, large-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 the 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 large-grained material with or without hydrogen and a slight decrease in total deformation was obtained for both cases.

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(2) R. L. Mehan and F. W. Wiesinger, "Mechanical Properties of Zircaloy-2," KAPL-2110, February 1, 1961.

(3) R. E. Reed-Hill, "An Evaluation of the Role of Deformation Twinning in the Plastic Deformation of Zr," Quarterly Report No. 2, USAEC-SROO, January, 1962.

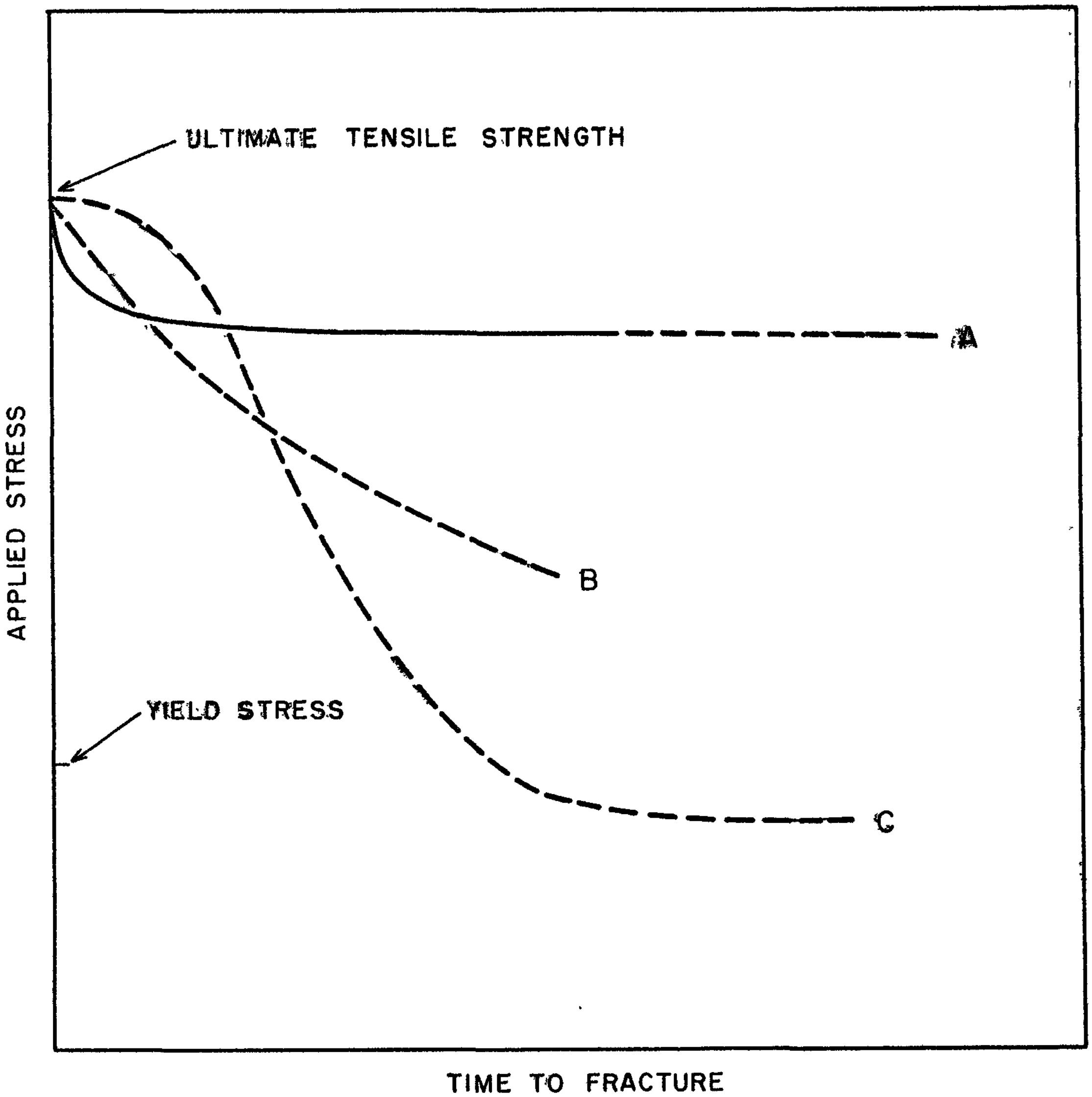
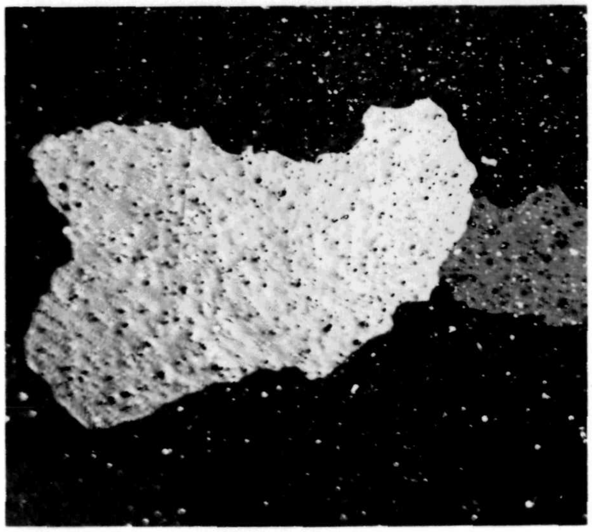


FIG. 1 - SCHEMATIC REPRESENTATION OF STATIC FATIGUE TESTS ON VARIOUS MATERIALS CONTAINING HYDROGEN

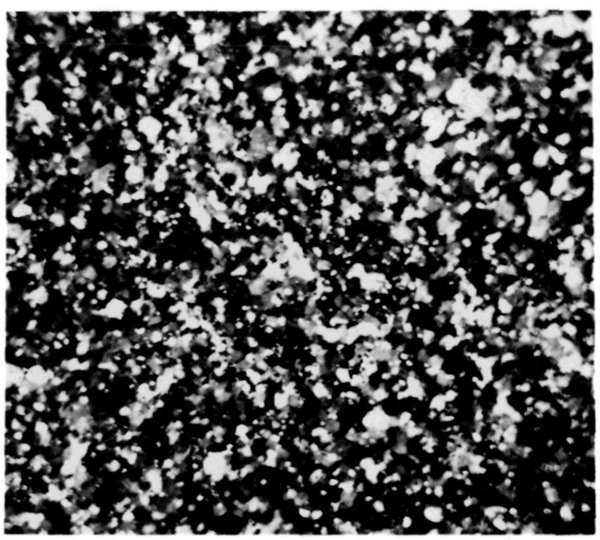
A. Zirconium and Zircaloy-2; This Investigation
B. Some Titanium Alloys
C. High-Strength Steels



Neg. No. 22561 Mag. X50

Figure 2

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



Neg. No. 22562 Mag. X50

Figure 3

Zircaloy-2, As-received and annealed at 800° C for 65 hours. No grain growth was observed. Polarized light.
Etchant: 1HF-1HNO_3 - 3 glycerin

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Large-grained, notched specimens of Zircaloy-2 containing 500 ppm hydrogen have recently been loaded for delayed failure studies. Thus far, the behavior appears similar to fine-grained material in that fracture occurred shortly after loading to stresses just below the ultimate stress whereas no failures have been observed in 200 hours at stresses more than 10, 000 psi below the ultimate.

Some rather disconcerting evidence for delayed failure of Zircaloy-2 has recently been provided by Ostberg.[4] In one particular batch of Zircaloy-2 containing about 100 ppm hydrogen, he claims to have observed delayed failure. The curve of applied stress versus fracture time is similar to that for titanium represented in Figure 1; data were given for times up to 1660 hours where fracture occurred at a stress approximately 25, 000 psi below the ultimate strength. However, Ostberg has not been able to duplicate these results in other batches of Zircaloy-2; he has not observed, at last report, any significant compositional differences between materials and is unable to associate the phenomenon with any physical or metallurgical parameter. Nonetheless, the slope of the curve definitely indicated delayed failure, and there was no evidence of asymptotic approach to a lower critical stress as observed for steel.

Because of this evidence, the present program is involved in evaluating lots of Zircaloy-2 sheet produced by various organizations. The material used thus far was supplied by the Wah Chang Corporation; more recently, an order for a small quantity of sheet has been placed with Reactive Metals Inc., and material furnished by Bettis Atomic Power Laboratory has already been evaluated. The BAPL material was slightly stronger than Wah Chang Zircaloy-2 and was more notch sensitive. At the 500 ppm hydrogen level, however, delayed failure was not observed.

IV. FUTURE WORK

It is known that the strength level of a steel affects the delayed failure characteristics. With a higher yield stress, for example, there is a greater amount of stored strain energy available for crack propagation; as

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(4) G. Ostberg, Aktiebolaget Atomenergi, Stockholm, Sweden; visit to ARF and private communication.

a result, such a material is more susceptible to delayed failure. In the light of this analysis, higher strength zirconium alloys will be investigated--in particular, Zr-2.5Nb.

In the fabrication of pressure tubes and certain in-core structural elements, very often as much as 20 per cent cold deformation is used in finishing. Such techniques might affect the susceptibility to delayed failure; during the next quarter, the effect of cold deformation on sensitivity to delayed failure will be determined.

Temperature has a strong influence on mechanical properties and, to some extent, probably affects delayed failure characteristics. Interpretation of dynamic tensile properties as a function of temperature, however, indicates that ambient reactor temperatures for a pressurized water system would probably not increase the susceptibility to delayed failure. Nevertheless, such studies ought to be conducted. Subzero temperatures, on the other hand, might promote delayed failure; however, the experimental difficulties associated with maintaining subzero temperature over a long period of time allow only a cursory study; such an experiment will be considered.

At present, a number of Zircaloy-2 specimens have been exposed to 750°F steam for 1200 hours. Static fatigue tests will be carried out on these specimens and further work will be initiated in this area. These specimens will contain a greater amount of oxygen than previous materials and will demonstrate any effect of oxygen on delayed failure characteristics. The application of stress during hydrogenation, which should cause concentration of hydrogen at the region of maximum triaxiality, is being considered for investigation in the near future.

V. CONCLUSIONS

An investigation is being pursued for the purpose of determining the degree of susceptibility of zirconium and zirconium alloys to delayed failure as caused by hydrogen absorption and applied stress. Data on unalloyed zirconium and Zircaloy-2 containing 200 ppm and 500 ppm hydrogen indicate that these materials are relatively insensitive to time-dependent fracture at room temperature. A greatly enlarged grain size does not, as yet, appear to promote static fatigue failure, and the introduction of a sharp notch does not cause fracture at reduced applied stresses.

VI. 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 are the following:

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

Respectfully submitted,

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