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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

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

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RESEARCH DESIGNED TO EVALUATE Zr-2.5Nb
AND Zr-2.5Nb-0.5Cu ALLOYS FOR DELAYED
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ABSTRACT

The purpose of this program is 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 by means of a modified Sieverts apparatus, heat treated or cold (150°C) reduced, and then evaluated in dynamic tensile and delayed failure tests.

Data presented on the ternary alloy show that the beta-quenched and aged condition is the most sensitive to static fatigue fracture. At room temperature, unnotched specimens containing 500 ppm hydrogen showed the ordinary dynamic tensile stress-strain curve with rather good properties for a zirconium alloy. However, at an applied stress of 95 per cent of the yield stress, static fracture occurred after several hundred hours. Other data are presented which indicate that this material is generally susceptible to static fatigue; however, additional work is necessary for more confident conclusions.

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I. INTRODUCTION

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

Delayed failure (or static fatigue) is the term applied to the time-dependent fracture of a material due to the combined effects of absorbed hydrogen and applied stress. 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.

While it has been known for quite some time that the presence of hydrogen in zirconium causes impact embrittlement and loss in tensile ductility, only recently has the delayed failure susceptibility of zirconium and zirconium alloys been studied. Investigations performed last year under the Collaborative Program showed that the high-strength alloy Zr-1.25Al-1Sn-1Mo containing 500 ppm hydrogen was highly susceptible to delayed failure at room temperature. Simultaneously, Ostberg in Sweden (by communication with ARF) indicated that Zircaloy-2 was sensitive to static fatigue in at least one isolated batch of material. More recently, he indicates that delayed failure has occurred in several instances in addition to the Zircaloy in which it was first observed. He does not make clear what conditions are necessary or whether he has been working with other alloys or other Zircaloy-2. In any case, existence of the static fatigue phenomenon in hydrided zirconium alloys has been established.

The alloy Zr-2.5Nb was studied during last year's program. In the quenched and tempered condition and with 500 ppm hydrogen, the material was only moderately susceptible to delayed failure but highly notch

sensitive at room temperature. Cursory evaluation at 2000 ppm hydrogen content showed that static fracture sensitivity was markedly increased. This alloy, or the modification Zr-2.5Nb-0.5Cu, is intended for use as pressure tube material in the heavy-water moderated and cooled reactor. As a result of corrosion, a certain amount of hydrogen will be absorbed during the operating lifetime (about 20 years). Thus, the present program aims for evaluation of delayed failure susceptibility of Zr-2.5Nb and Zr-2.5Nb-0.5Cu under various conditions of hydrogen content, heat treatment, temperature, and metallurgical history.

II. EXPERIMENTAL

The apparatus used in this program, the specimen design, and the experimental procedures were outlined in Quarterly Report ARF B6005-2; only a brief review of certain procedures and of work scope will be given here.

The scope of work to be performed during the current year includes study of Zr-2.5Nb and Zr-2.5Nb-0.5Cu with three different metallurgical histories: fully annealed, annealed and cold worked, and beta-quenched and tempered. For these conditions, delayed failure evaluation will be performed at room temperature, 250° C, and 300° C, and the specimens will be vacuum annealed or will contain 200 ppm and 500 ppm hydrogen. The applied stress will be 95 per cent of the yield strength (at temperature) as determined by dynamic tensile tests. Thus, approximately 250 specimens are to be evaluated during the current year.

During this quarter, specimen preparation, tensile evaluation, and delayed failure tests have proceeded without experimental difficulty. The ternary alloy has been received from the Chalk River Laboratory as 1/2 inch diameter rods which are cut to specimen size (3 inches) and then hydrogenated at 500° C for 24 hours in a modified Sieverts apparatus. The amount of hydrogen added to each specimen is known, and weight gain is used to check each specimen for hydrogen concentration. Following hydriding, specimens are appropriately heat treated in sealed, helium-filled, vycor capsules. Unnotched specimens are machined with a 1 1/4 inch long, 0.200 inch diameter

gage length; notched specimens are cut with a 45°V-notch and then slotted with a 0.001 inch abrasive-coated wire ($K_t = 8$). Dynamic tensile tests are carried out on a 10,000-pound capacity Instron machine using a cross-head speed of 0.05 inches/minute.

One condition for specimen evaluation consisted of beta-annealing for 15 minutes, furnace cooling, and then 30 per cent cold reduction by swaging. When the material (ternary) contained hydrogen, swaging at room temperature caused surface cracking or, in some cases, internal center cracking along the specimen axis. If swaging is performed at 150° C, however, no cracking is observed. The microstructure showed evidence of plastic deformation extending to the center of specimens and no recrystallization was observed. For evaluation of specimens in the annealed and cold worked condition, therefore, swaging has been carried out at 150° C rather than room temperature.

III. RESULTS AND DISCUSSION

Data obtained thus far on the ternary alloy are presented in Tables I through IV; both the dynamic tensile properties and delayed failure evaluations are outlined for a given condition of heat treatment.

A. Table I: 825° C, 1/4 hr--> Furnace Cooled

Base properties of this material in the annealed condition are represented by data on unnotched, vacuum annealed specimens. The normal tensile stress-strain curve was obtained, and static testing at an applied stress of 95 per cent of the yield stress did not result in failure within 1000 hours. When 500 ppm hydrogen was added to this specimen, the strength was increased and the ductility was decreased. When static load is applied, no susceptibility to delayed failure is observed. If the specimen is now notched, the dynamic tensile properties are somewhat changed. A straight line to fracture is observed on the load-elongation curve, and yield stress cannot be calculated. Further, the introduction of a notch does not allow for ductility determinations. However, the "notch sensitivity" is usually employed as a somewhat empirical criterion for plastic deformation under the influence of a notch. If the ratio of notched tensile strength to unnotched

TABLE I
DYNAMIC TENSILE AND DELAYED FAILURE
EVALUATION OF Zr-2.5Nb-0.5 Cu ANNEALED
AT 825° C, 1/4 HR --> FURNACE COOLED

Condition	Ultimate Tensile Strength, psi	Yield Stress, psi (0.2% offset)	Elongation, %	Applied Stress, psi	Time to Failure, hr
Room Temperature, Unnotched, Vacuum Annealed	74,000	43,400	30.8	41,300	*
Room Temperature Unnotched, 500 ppm H ₂	79,400	58,900	15.5	55,900	*
Room Temperature Notched, 500 ppm H ₂	79,700	--	--	75,600	94
250° C, Unnotched, Vacuum Annealed	52,400	29,400	33.6	27,900	733.4
250° C, Unnotched, 500 ppm H ₂	49,800	37,300	12.4	35,500	*
250° C, Notched, 500 ppm H ₂	98,800	--	--	93,700	0.01

* No fracture within 1000 hours

-- Load-elongation curve showed straight line to fracture.

tensile strength is less than 1, then the material is said to be notch sensitive. Thus, the tensile strength of this material with a notch is about the same as the strength in the unnotched condition; the material is not notch sensitive. However, there is apparently some sensitivity to static fatigue failure with introduction of a notch. Fracture was observed after 94 hours at an applied stress of 75,600 psi. The fracture was not of the cleavage type and, undoubtedly, some plastic deformation occurred prior to fracture. A better evaluation of delayed failure sensitivity will require additional specimens tested at progressively lower applied stresses.

At 250° C, the dynamic tensile properties are about similar to those obtained at room temperature. The unnotched vacuum annealed specimen failed in a static test after 733.3 hours due to creep; severe necking of this specimen was observed. The notched specimen fractured on loading, and it is difficult to tell if this was due to creep or delayed failure. From past experience, a material which is sensitive to static fatigue will exhibit fracture in both notched and unnotched specimens. In this case, the unnotched specimen containing 500 ppm hydrogen did not fracture.

B. Table II: 825°C, 1/4 hr. -> Furnace Cooled, Swaged 30% at 150° C

Dynamic tensile data for material in this condition show that cold working markedly increases strength and reduces ductility; the unnotched specimen with 500 ppm hydrogen, however, did not exhibit static fracture. When the specimen is notched, a low tensile fracture stress is observed (notch sensitive), and static loading at 95 per cent of this stress resulted in failure in 7.9 hours. An identical specimen loaded at 76 per cent of the notched tensile fracture stress failed in 330 hours. It appears that the ternary alloy in the cold worked condition is sensitive to delayed failure when influenced by a notch. At 250° C, the material is not notch sensitive when it contains 500 ppm hydrogen. Static fracture was observed on loading a specimen to 95 per cent of the notched tensile fracture stress; however, this behavior could be due to creep, scatter in tensile properties, or possibly delayed failure. Additional work is necessary to establish the mode of failure.

TABLE II
DYNAMIC TENSILE AND DELAYED FAILURE EVALUATION
OF Zr-2.5Nb-0.5Cu ANNEALED 825° C,
1/4 HR --> FURNACE COOLED; SWAGED 30% AT 150° C

Condition	Ultimate Tensile Strength, psi	Yield Stress, psi (0.2% offset)	Elongation, %	Applied Stress, psi	Time to Failure, hr
Room Temperature, Unnotched, 500 ppm H ₂	102,700	79,000	7.4	75,000	*
Room Temperature, Notched, 500 ppm H ₂	85,400	--	--	81,000	7.9
Repeat of Above	--	--	--	65,000	330
250° C, Notched, 500 ppm H ₂	142,000	--	--	134,800	0.01

* No fracture within 1000 hours

-- Load-elongation curve showed straight line to fracture.

C. TABLE III: 825° C, 1/4 hr --> Water Quenched; Aged
535° C, 6 hr --> Air Cooled

In the quenched and tempered condition, the tensile properties of Zr-2.5Nb-0.5Cu are generally very good; the tensile strength was increased by this heat treatment to almost 117,000 psi while maintaining about 15 per cent tensile elongation. For a zirconium alloy, these properties are quite good. In the unnotched, vacuum annealed condition, static failure was not observed. With the addition of 500 ppm hydrogen, the dynamic tensile properties are not significantly changed, perhaps due to the fact that a large amount of the hydrogen exists in solid solution with beta. However, the alloy appears to be highly susceptible to delayed failure; this unnotched specimen fractured in 733.6 hours at an applied stress below the tensile yield stress. Figure 1 (top) shows that very little plastic deformation accompanied fracture, yet the fracture surface is not of the cleavage type with smooth faces. It is fairly certain that fracture was initiated by cracks first forming at the surface, as can be seen in Figure 2. Such behavior is characteristic of delayed failure of steels and static fatigue of the zirconium alloy studied last year. (It is interesting to note that the alloy Zr-1.25Al-1Sn-1Mo, highly susceptible to delayed failure, did not show hydride formation in the microstructure; the hydrogen was in solid solution with beta. Weinstein and Holtz, in a paper submitted to ASM, suggested that delayed failure was due to stress-induced hydride precipitates at alpha/beta interfaces, just as in the case of alpha/beta titanium alloys. In the present alloy, it is possible that a similar mechanism is operative since some of the hydrogen exists in beta. A feathery, acicular phase also exists in the microstructure which, by etching techniques developed at Savannah River Laboratory, has been identified as zirconium hydride. The amount of this phase, however, is less than what has been observed when the total hydrogen content exists as hydrides.)

The remaining data reported in Table III are not significantly different from what one might expect. The notched specimen, of course, also exhibited static fracture. At 250° C, the unnotched, vacuum annealed specimen failed by creep in the severely necked-down portion of the specimen. One suspects that this particular specimen might not have been properly heat treated.

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TABLE III
DYNAMIC TENSILE AND DELAYED FAILURE EVALUATION
OF Zr-2.5Nb-0.5Cu ANNEALED 825° C,
1/4 HR--> WATER QUENCHED; AGED 535° C, 6 HR--> AIR COOLED

Condition	Ultimate Tensile Strength, psi	Yield Stress, psi (0.2% offset)	Elongation, %	Applied Stress, psi	Time to Failure, hr
Room Temperature Unnotched, Vacuum Annealed	116,800	102,900	14.8	97,700	*
Room Temperature Unnotched, 500 ppm H ₂	116,000	102,500	13.4	97,400	733.6
Room Temperature Notched, 500 ppm H ₂	90,000	--	--	85,500	0.01
250° C, Unnotched, Vacuum Annealed	90,000	79,100	17.0	75,100	5.7
250° C, Unnotched, 500 ppm H ₂	89,500	84,500	14.2	80,300	*
250° C, Notched 500 ppm H ₂	168,000	--	--	159,000	0.01

* No fracture within 1000 hours

-- Load-elongation curve showed straight line to fracture.

Neg. No. 24804

Fig. 1

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

Top: 825° C, 1/4 hr → W. Q.; aged 535° C,
6 hr → A. C. time to fracture = 733.6 hr.

Bottom: 825° C, 1/4 hr → W. Q.; aged 400° C,
6 hr → A. C. time to fracture = 378.7 hr.

Neg. No. 24807

Mag. X17

Fig. 2

Area at fracture of Zr-2.5Nb-0.5Cu with 500 ppm hydrogen; beta quenched (825° C) and aged at 535° C; statically loaded (room temperature) at 95 per cent of the dynamic tensile yield stress. Time to fracture = 733.6 hr. Note crack formation (arrows) at surface of specimen.

D. Table IV: 825° C, 1/4 hr--> Water Quenched; Aged
400° C, 6 hr--> Air Cooled

The lower temperature aging treatment caused a further increase in strength with only slightly reduced ductility. The unnotched, vacuum annealed specimen failed on loading to a stress of 95 per cent of the yield stress; severe necking of the specimen was observed. Such results are rather disconcerting; perhaps an error was made in calculations, or heat treatment of that particular specimen was not properly performed. Figure 1 (bottom) shows the static fatigue fracture of the unnotched specimen with 500 ppm hydrogen. Just as in the case of material aged at 535° C, very little plastic flow accompanied fracture, and surface cracks are apparent. That fracture occurred below the yield stress suggests that this material is highly sensitive to static fatigue. The material is also notch sensitive. Instantaneous static fracture occurred at an applied stress of 95 per cent of the notched tensile fracture stress; an additional specimen loaded at 85 per cent of the fracture stress failed in 243.7 hours. At 250° C, no fractures have yet been observed.

Thus far, very little significant data are available on the binary Zr-2.5Nb alloy; limited exploratory work was performed on this material, and only a few results have been obtained on the small amount of material which was available. A specimen in the notched, annealed condition (880° C, 1/4 hr--> furnace cooled) containing 500 ppm hydrogen fractured in 167.1 hours at an applied stress of 95 per cent of the tensile fracture stress (straight line to fracture). Additional studies must be carried out in order to reach valid conclusions.

The last Quarterly Report (ARF-B6005-2) described rather cursory investigations on delayed failure of Zircaloy-2 containing hydrides oriented perpendicular to the stress axis. Apparently, certain statements made therein were rather misleading. The results obtained were hardly conclusive but in general, it appears that hydride orientations affect delayed failure susceptibility. In order to investigate this effect properly, single long specimens must be used from which two specimens are prepared, one for dynamic tension and one for static fatigue. By this method, experimental

TABLE IV
DYNAMIC TENSILE AND DELAYED FAILURE EVALUATION
OF Zr-2.5Nb-0.5Cu ANNEALED 825° C,
1/4 HR--> WATER QUENCHED; AGED 400° C, 6 HR--> AIR COOLED

Condition	Ultimate Tensile Strength, psi	Yield Stress, psi (0.2% offset)	Elongation, %	Applied Stress, psi	Time to Failure, hr
Room Temperature, Unnotched, Vacuum Annealed	144,300	132,200	12.0	125,200	0.01
Room Temperature, Unnotched, 500 ppm H ₂	139,200	128,500	6.9	122,200	378.7
Room Temperature, Notched, 500 ppm H ₂	88,800	--	--	84,300	0.01
Repeat of Above	--	--	--	75,000	243.7
250° C, Unnotched, Vacuum Annealed	107,500	98,800	13.0	93,900	*
250° C, Unnotched, 500 ppm H ₂	106,700	94,000	10.8	89,200	*

* No fracture within 1000 hours

-- Load-elongation curve showed straight line to fracture.

scatter is greatly reduced. An investigation of the required magnitude is beyond the scope of the present program, and further studies will not be carried out. A separate program for this work has been proposed.

IV. FUTURE WORK

A 15 foot rod of Zr-2.5Nb-0.5Cu has been received, and work is proceeding to study further the delayed failure of this material under various conditions. With the presently available material, practically all of the desired conditions will have been covered. But it should be apparent from the data presented that to describe confidently the static fatigue behavior for a certain set of conditions, a number of specimens are required. When the present ternary investigations are completed, the possibility of more detailed study for certain conditions ought to be considered. Additional work to be performed during the next quarter will attempt to correlate microstructure with fracture characteristics.

As yet, rods of Zr-2.5Nb have not been received. When this material is available, work similar to that on the ternary alloy will proceed.

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 probably not sensitive to delayed failure with up to 500 ppm hydrogen. The introduction of a notch might promote static fatigue susceptibility, but more data are necessary to confirm this possibility. For specimens which were annealed and swaged (30 per cent reduction at 150°C), notched specimens containing 500 ppm hydrogen exhibited failure (330 hours) at an applied stress of 75 per cent of the fracture stress. In the beta-quenched and aged condition, the sensitivity to delayed failure is such that fracture is observed at room temperature in unnotched specimens at applied stress of 95 per cent of the tensile yield stress (500 ppm hydrogen). Thus, while this heat treatment yields the best dynamic mechanical properties (as well as required corrosion resistance), it is

perhaps the least desirable from the standpoint of delayed failure. In general, considerably more data are necessary to establish more firmly the delayed failure sensitivity of this material.

VI. LOGBOOKS AND CONTRIBUTING PERSONNEL

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

Personnel contributing to this work are the following:

L. J. Adamski	-	Project Technician
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Respectfully submitted,

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