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CORROSION AND HYDRIDING OF ZIRCALOY

— Task 2 Final Report —

Effects of Hydrogen and Precipitated Hydrides on Mechanical Properties of Zircaloy-4

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SUMMARY

Zircaloy fuel cladding in water reactors is required to serve for 1000 days or more in pressurized or boiling water at temperatures from 550 to 650 F. The cladding is also expected to transfer heat at surface heat fluxes as high as 650,000 Btu/hr-ft^2 and to act as an integral structural component in the fuel bundle. To accomplish these tasks efficiently, the material must have excellent corrosion resistance and strength. The designer of fuel cladding requires reliable data on the corrosion and strength properties of the material over the anticipated range of operating conditions. Any changes in these properties during the service period must be factored into the initial design to assure the reliability required for cladding service.

The hydrogen effects portion of the Corrosion and Hydriding Test Program was initiated to determine how the strength of Zircaloy fuel cladding is affected by the absorption of hydrogen during service. It was estimated that as much as 25 mg/dm^2 of the hydrogen released by corrosion could be absorbed during a 1000-day service life. This would amount to more than 500 parts per million hydrogen in 25-mil cladding. Therefore, the scope of the program was established to determine the tensile properties of Zircaloy tubing containing up to 1000 ppm hydrogen over a temperature range from 70 to 800 F. (1000 ppm hydrogen is an estimated possible local concentration under severe operating conditions, and 800 F corresponds to the calculated inside diameter temperature under peak operating conditions toward the end of the core life.) Burst tests of hydrided material were included, but these were limited to room-temperature testing. Annealed and cold-worked material from the same lot of Zircaloy tubing was tested.

Tensile tests were performed at six different temperatures, including the extremes of 70 and 800 F, and six different hydrogen concentrations were established as test parameters. Three specimens were

tested at each condition, resulting in a total of 108 annealed and 108 cold-worked specimens tested. Since burst tests were performed only at room temperature, 18 annealed and 18 cold-worked specimens were sufficient.

The tensile-test results show that hydrogen has no significant effect on the tensile and yield strength of Zircaloy over the 70 to 800 F temperature range. On the other hand, tensile elongation is reduced appreciably at temperatures below 300 F. Significant reductions in tensile elongation persist over the entire temperature range of interest when the hydrogen concentration is above 200 ppm. These results show that at operating temperatures, residual ductility measured by tensile elongation is consistently above 10% for cold-worked material containing as much as 1000 ppm hydrogen. However, at low temperatures, elongation values as low as 3% were measured, which indicates that post-operation handling of fuel elements will require care to avoid shock loading or imposed strains that could breach the cladding.

The results of burst testing show that hydrogen reduces room-temperature (70 F) burst strength and ductility. Under the biaxial loading conditions of the test, the burst strength of cold-worked Zircaloy-4 tubing was reduced about 25% (from 115,000 to 85,000 psi) by adding 1000 ppm hydrogen to the test specimens. The burst strength of annealed tubing was reduced about 18% (from 88,000 to 72,000 psi) by the same hydrogen addition. Significant fragmentation of both the annealed and cold-worked tubing occurred on bursting; this indicates a low ductility and confirms the need for careful handling of hydrided fuel elements.

Further testing is needed to quantify the effects of hydrogen on the elevated-temperature burst strength of Zircaloy. The initial tests indicated that hydrogen is detrimental to the burst strength of the material at room temperature, and elevated-temperature data are required to factor this loss of strength into the fuel element design.

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1. INTRODUCTION

Fuel cladding in pressurized and subcritical-pressure boiling-water reactors is generally made of the zirconium-tin alloys Zircaloy-2 or Zircaloy-4. These alloys exhibit the strength and corrosion resistance necessary to withstand the rigors of reactor service, and their nuclear properties are much superior to those of other available materials.

There is a continuing effort to increase the thermal performance of water reactors by increasing the operating temperatures, heat flux, and service life. Intermittent relocation of the fuel elements in the reactor core further adds to the severity of service conditions by introducing a potential high-strain-fatigue factor over and above the cyclic stresses of normal service. Although operational experience with Zircaloy has been excellent,[1] some failures of experimental Zircaloy-clad fuel elements indicate that operational limitations must be defined precisely before a Zircaloy-clad core is committed to the demanding conditions of some of the more advanced reactor designs.

The Zircaloy tubing specified for fuel cladding service in pressurized and boiling-water reactors must exhibit and retain tensile properties greater than those of annealed material. During operation, however, the fuel cladding is subjected to the hardening effects of radiation, the annealing effects of prolonged exposure at elevated temperature, and the ill-defined effects of the increased hydrogen content caused by absorption of part of the corrosion-released hydrogen. Operational and lifetime limitations have been placed on Zircaloy-clad elements because of the postulated effects of hydrogen on the mechanical properties necessary to maintain cladding integrity. The limitations are artificial, since they did not result from failure experience or from systematic experimental determinations of the effects of hydrogen on these properties.

The objectives of this program are to define better the effects of hydrogen on the mechanical properties of Zircaloy-4 and to evaluate these effects with respect to overall performance limitations for Zircaloy fuel cladding.

During a previous experimental program at B&W,[2] it was shown that hydrogen (in the form of a hydride case up to about 0.001 inch thick or uniformly distributed at a concentration up to about 350 ppm) has no significant effect on the tensile or burst strength of 0.420-inch-diameter, 0.025-inch-wall, cold-worked Zircaloy-4 tubing. Tensile elongation values for hydrided specimens were not significantly lower than the elongation values for unhydrided specimens. The innocuous effect of hydrogen on strength and longitudinal ductility indicates that there is little experimental or practical basis for limitations on hydrogen concentrations.

The ductility during burst testing was appreciably lower in the uniformly hydrided specimens than in the specimens with hydride rims or the unhydrided specimens. The fracture in the burst specimens also exhibited the embrittling effects of precipitated hydride in Zircaloy. The unhydrided and electrolytically hydrided specimens, where the hydrogen is concentrated in a layer or case at the outside surface, displayed considerable deformation before fracture, and the fractures were relatively short. The specimens with uniformly distributed hydride were only slightly deformed, and the fractures had propogated in a brittle fashion almost the full length of the specimens.

2. PROGRAM DESCRIPTION

The test program was designed to provide more accurate data on how the tensile and burst properties of annealed and cold-worked Zircaloy-4 tubing are affected by hydrogen. Hydrogen concentrations of 20 ppm (representative of as-received material) to 1000 ppm were studied. The test temperatures for the tensile specimens were from 70 (room temperature) to 800 F; burst testing was conducted at room temperature only.

Table 1 lists the kinds of tests performed on each series of specimens. The tensile tests provide data for evaluating strength and ductility as functions of hydrogen content and temperature for both cold-worked and annealed material. The burst tests provide data to illustrate the effects of hydrogen on the biaxial strength of Zircaloy-4 tubing.

Table 1. Test Parameters

Tensile Tests		
Material conditions:	Annealed Cold-worked	
Hydrogen content, ppm:	20 150 350 500 750 1000	
Test temperature	F	C
	70	21
	250	121
	500	260
	650	343
	700	371
	800	427
Specimens per test condition:	3	
Total tensile specimens tested:	216	

Burst Tests

Tested at room temperature only; all other parameters were the same as those for the tensile tests.

Total burst test specimens: 36

3. EXPERIMENTAL PROCEDURE

3.1. Specimen Preparation

The Zircaloy-4 tubing for this test program was cold-reduced to the finish size of 0.422-inch OD by 0.277-inch wall thickness using the tube-reducing process. The final cold-reduction was performed to work-harden the tubing enough to meet the strength specifications after stress relieving (tempering) for at least one hour at a temperature above 900 F (480 C). The chemical analysis and the results of nondestructive inspections and mechanical properties tests on the specimen material are shown in the mill test reports in the appendix. The annealed specimens were produced by annealing part of the cold-worked tubing in a vacuum furnace at 1450 F (788 C) for one hour followed by furnace cooling.

For testing convenience, full tube specimens approximately 30 inches long, rather than strip specimens machined from the tubing, were used for tensile testing. The burst-test specimens were sections of tubing 6 inches long. Mechanical fittings were used to close off one end of the burst-test specimens and to connect the other end to the burst-test apparatus.

3.2. Hydriding Procedure

Previous hydriding experience indicated that gas hydriding to the high hydrogen content required for this test program would take as long as 72 hours if temperatures were kept low enough to prevent reducing the strength of the cold-worked cladding. Winton reported a method for gas hydriding zirconium alloys in which a low partial pressure of carbon tetrachloride is added to the furnace before the hydrogen is added.[3] The carbon tetrachloride disrupts the impervious oxide film and permits the hydrogen to react with the Zircaloy more rapidly. This procedure was followed because it reduced considerably the total time cycle for hydriding a batch of material and it did not require excessive temperatures.

Exposures at 750 F varied from 40 to 150 minutes, depending on the amount of hydrogen to be introduced.

Figures 1 and 2 are a photograph and a schematic diagram of the gas hydriding apparatus. The furnace is a heated 4-inch Inconel tube connected directly to a 4-inch vacuum diffusion pump. Material is charged into the furnace section by removing a blind flange. The hydrogen gas used for hydriding enters directly into the evacuated furnace from the gas bottle without additional purification. The argon used for purging the furnace before and after each hydriding operation is purified by passing it through hot zirconium chips before it enters the furnace.

Several hydriding cycles were run to standardize the procedure and to determine the variability of the hydrogen concentration between specimens in the same furnace charge and over the length of the 30-inch tensile specimens. Hydrogen analyses of several specimens from each furnace charge indicated consistent and uniform hydrogen pickup between specimens and between zones in the furnace. Figure 3 illustrates the variation in hydrogen content over the length of a 30-inch specimen. The apparent small decrease in the hydrogen content toward the end of the specimen is attributed to the slight variation in temperature profile over the length of the furnace. Since the hydrogen content is extremely uniform in the gage area of the specimen, property variations resulting from inhomogeneous hydrogen content should be minimal. Figure 3 also includes photomicrographs of various sections of the hydrided tube, showing the uniformity of the precipitated hydride over the length of the tube and the uniformity of the precipitate through the tube wall.

3.3. Hydrogen Analysis

The hydrogen analyses were performed on an apparatus using the hot-vacuum extraction process. National Bureau of Standards hydrided titanium standards were used to calibrate the analytical equipment. An accuracy of ±5% of the specified hydrogen content was attained consistently.

Table 2 is a summary of the hydrogen analyses. The average hydrogen content for any group of specimens is in good agreement with the amount of hydrogen introduced to the material. The maximum deviations are given to show the variations exhibited by various specimens.

Table 2. Summary of Hydrogen Analyses

Specified H_2 content, ppm	Avg H_2 content of specimens, ppm	Deviation of avg from specified, %	Maximum deviations from avg, ppm	
			Maximum	Minimum
		Annealed Material		
20	19	1	37	13
150	148	1.5	157	134
350	351	1	369	340
500	588	17.5[a]	611	437
750	749	1	807	613
1000	965	3	1066	924
		Cold-Worked Material		
20	17	1.5	27	11
150	149	1	166	135
350	149	1	364	330
500	540	2	585	522
750	743	1	770	711
1000	942	5	956	922

[a] An obvious error in the values for several specimens in this group caused the large deviation value shown.

3.4. Tensile Testing Procedure

Tensile testing was carried out on a 120,000-pound universal testing machine using a load range of 0 to 6000 pounds. The loading rate was controlled at 0.005 ± 0.002 inch per inch of gage length per minute. The elongation through the yield point was determined using an extensometer attached directly to the gage length of the specimens. The strain and corresponding load was automatically recorded past the yield point. The extensometer was removed after the yield strength had been exceeded, and the specimen was further loaded to fracture.

Elevated-temperature testing was performed in the same manner as the room-temperature tests, except that a high-temperature extensometer was used to record strain and a three-zone electrical-resistance furnace was used to heat the specimen. The furnace was controlled by the output from a thermocouple connected directly to the specimen.

To investigate the possibility that hydrogen could migrate away from the high-temperature gage section during tensile testing, the mechanical properties of a specimen intentionally aged for 45 minutes in the tensile-test furnace were compared with those of a specimen heated rapidly and tested within less than 5 minutes. Table 3 lists the results of this comparison.

Table 3. Effects of Aging at Test Temperature on 800 F Tensile Properties

	Without aging	Aged 45 min at 800 F
Ultimate strength, psi	51,800	56,250
Yield strength, psi	33,800	42,800
Elongation, % in 2 in.	12.5	12.5
Hydrogen content, ppm	365	355

Aging at 800 F had no effect on the tensile elongation of the specimen, but the yield and ultimate strengths were increased significantly. Figure 4 includes photomicrographs of both aged and unaged specimens. The hydride precipitates appear to have agglomerated during the aging treatment. Analyses for hydrogen variations over the length of the aged specimen indicated that no significant axial migration had occurred.

Experiments were also performed to establish the dwell time at testing temperature required to stabilize the hydride within the specimen so that the test results would be consistent. It was suspected that a definite time period would be required to dissolve precipitated hydrides, and that testing before dissolution to the solubility limit at the test temperature would produce erroneous results.

A series of specimens was hydrided to a level of 450 ppm hydrogen and then tested at 800 F after an aging treatment (at 800 F) of either 25 minutes or 24 hours. The effect of the aging treatment was negligible; however, there was an effect from dwell time at the testing temperature before testing the specimen. From these test results, shown in Figure 5, it was established that an aging treatment was not required and that a dwell time of 30 minutes before testing was adequate to stabilize the specimen so that reproducible data could be obtained.

3.5. Burst Testing Procedure

Previous experience with burst testing, which had been conducted at room temperature using water as the pressuring media, indicated that the system should be modified to produce more consistent results. Therefore, the burst-test facility was modified so that gas could be used as the pressuring media and more control could be exercised over the rate and uniformity of loading.

Figure 6 is a diagram of the burst-test facility. The accumulator is charged by a nitrogen bottle (through a check valve) to a pressure of 1500 to 2000 psi. The gas pressure in the gas-over-liquid accumulator is increased to 29,000 psi by pumping water into the bottom of the accumulator; the control valve releases the gas to the specimen. A metering valve controls the loading rate of the specimen, a high-precision peak-load pressure gage monitors the system pressure, and a strip-chart recorder records the rate of pressurizing the specimen. Figure 7 shows the burst-test specimen holder with the blast shield in the lowered position; the accumulator is at the right, and the pressure transducer is located at the top of the photograph. The mechanical fittings that seal the bottom end of the specimen and attach the specimen to the system are illustrated.

The burst strength of the specimen was calculated from the burst pressure using the following equation:

$$S = \frac{PD}{2t}$$

where

S = burst strength, psi
P = burst pressure, psi
D = inside diameter of tubing, inches
t = wall thickness of tubing, inches

A series of room-temperature burst tests was performed to determine the sensitivity of the burst strength of Zircaloy-4 to the rate of loading. These tests were conducted at loading rates from 134 to 2100 psi per second; the results are shown in Figure 8. Rupture was produced in the time range of 7.5 to 126 seconds. The varied loading rates produced no significant difference in the burst strength of the specimens. These results agree with the results of Mishima, who has reported similar behavior for the burst strength of Zircaloy-2.[4] As a result of these preliminary experiments, a loading rate of less than 200 psi per second was selected for the test program.

Figure 1. Gas-Hydriding Apparatus (WAS-67-830)

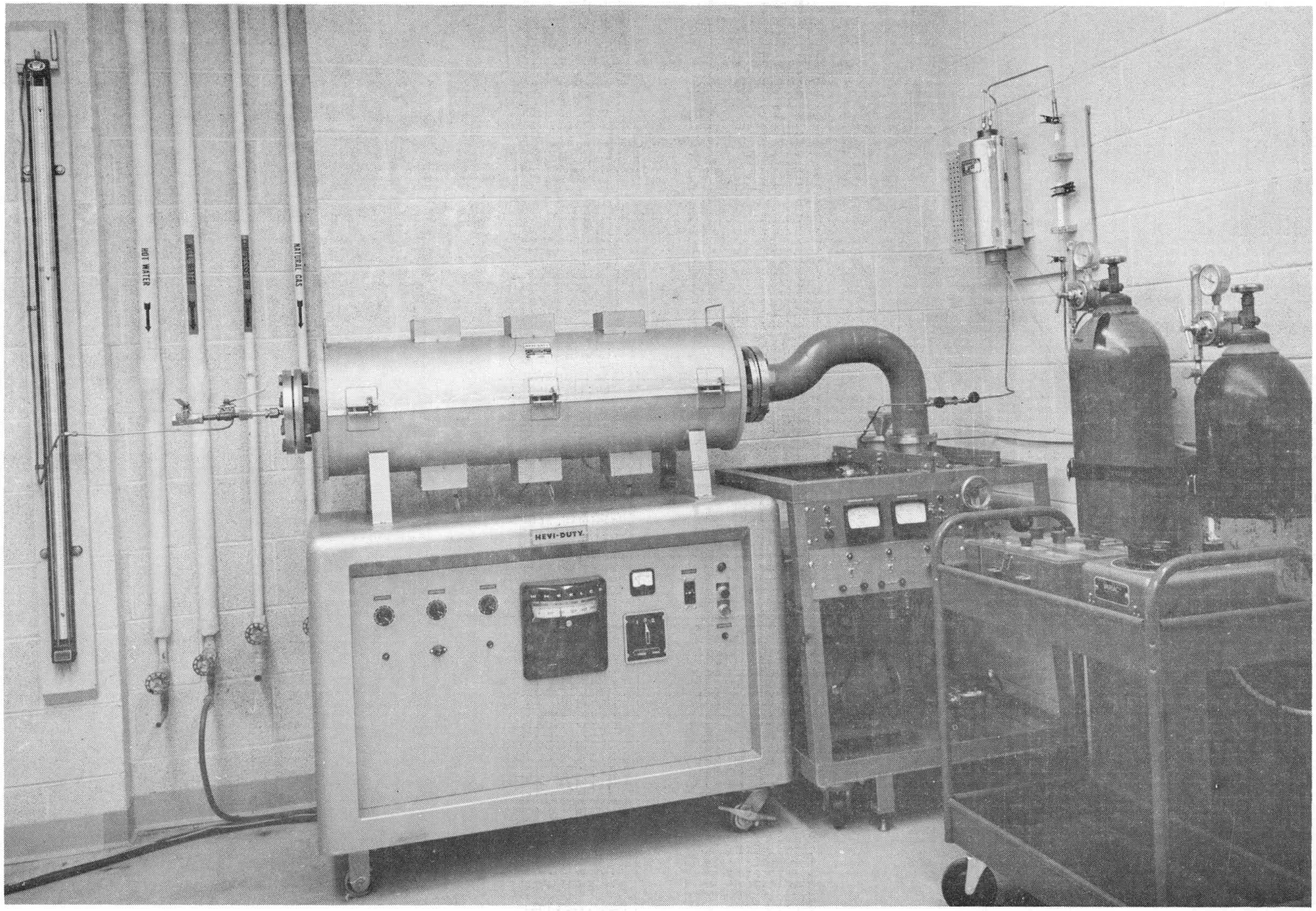


Figure 2. Diagram of Gas-Hydriding Apparatus

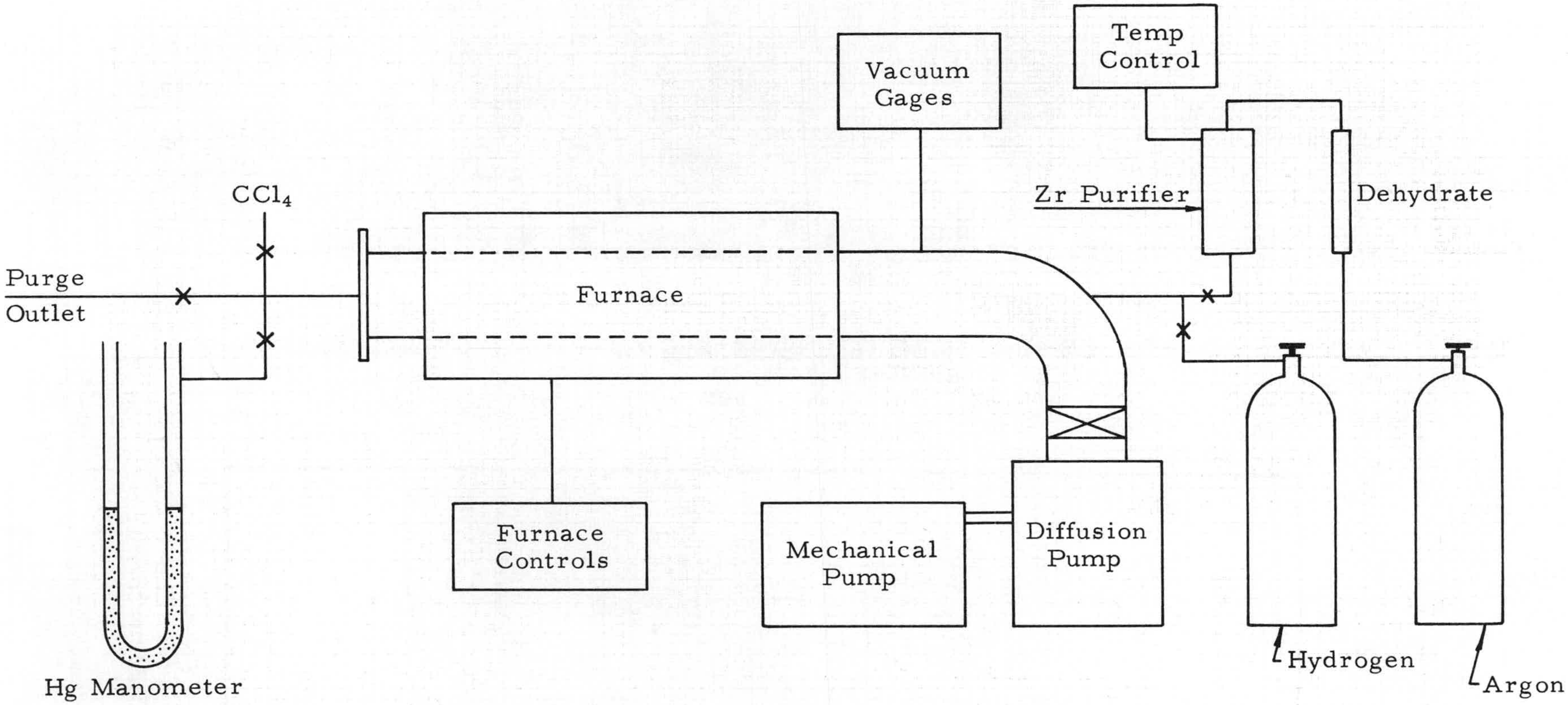
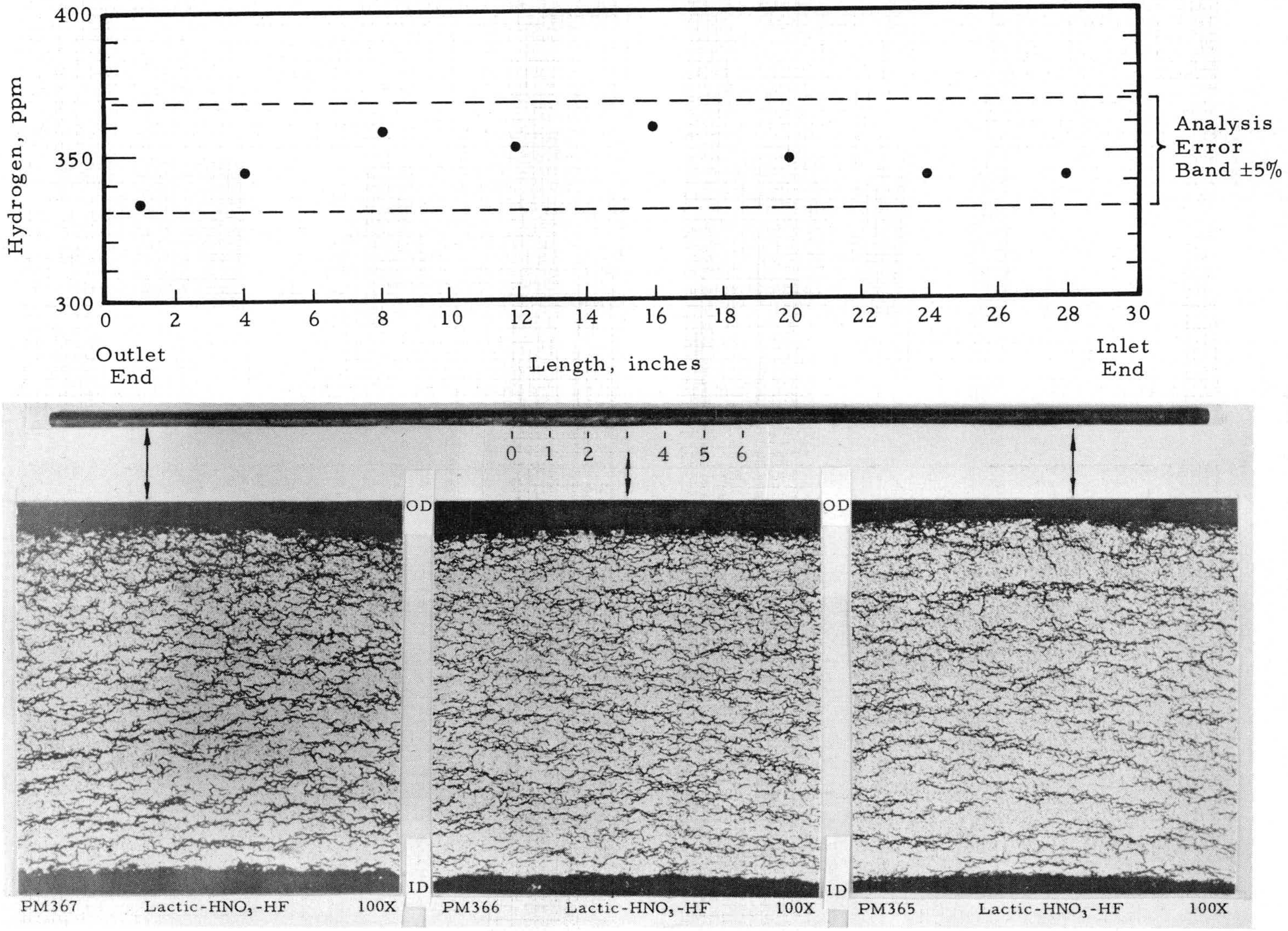


Figure 3. Hydrogen Concentration Variations in a 30-Inch-Long Tensile Specimen (reduced 15%)

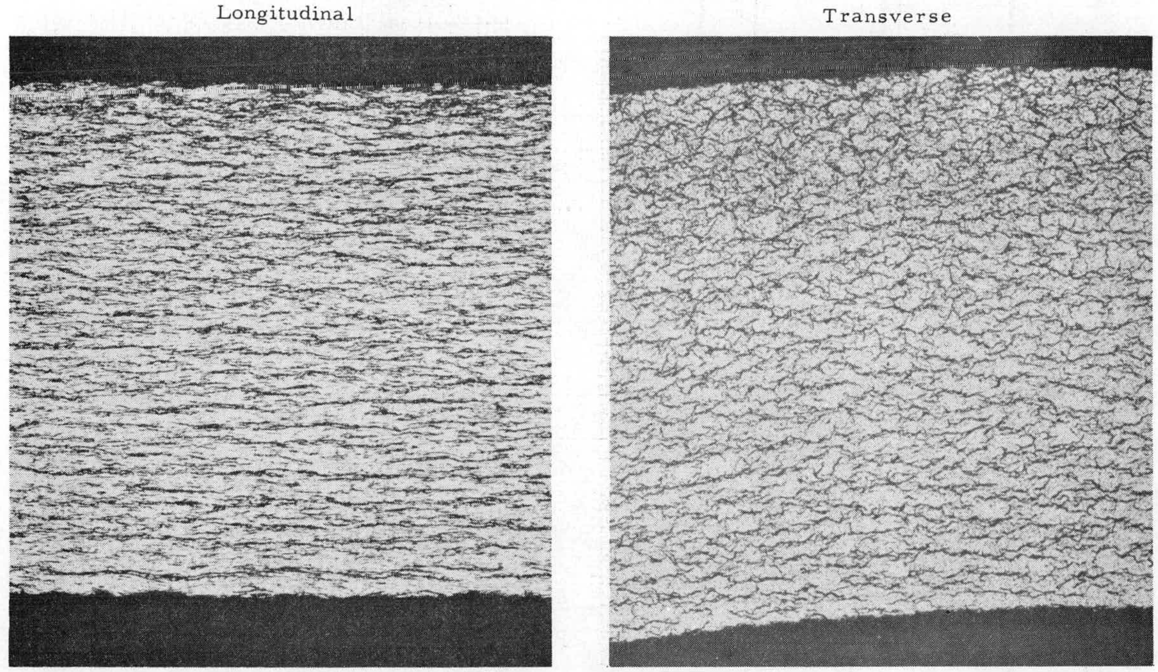


PM367 Lactic-HNO_3-HF 100X

PM366 Lactic-HNO_3-HF 100X

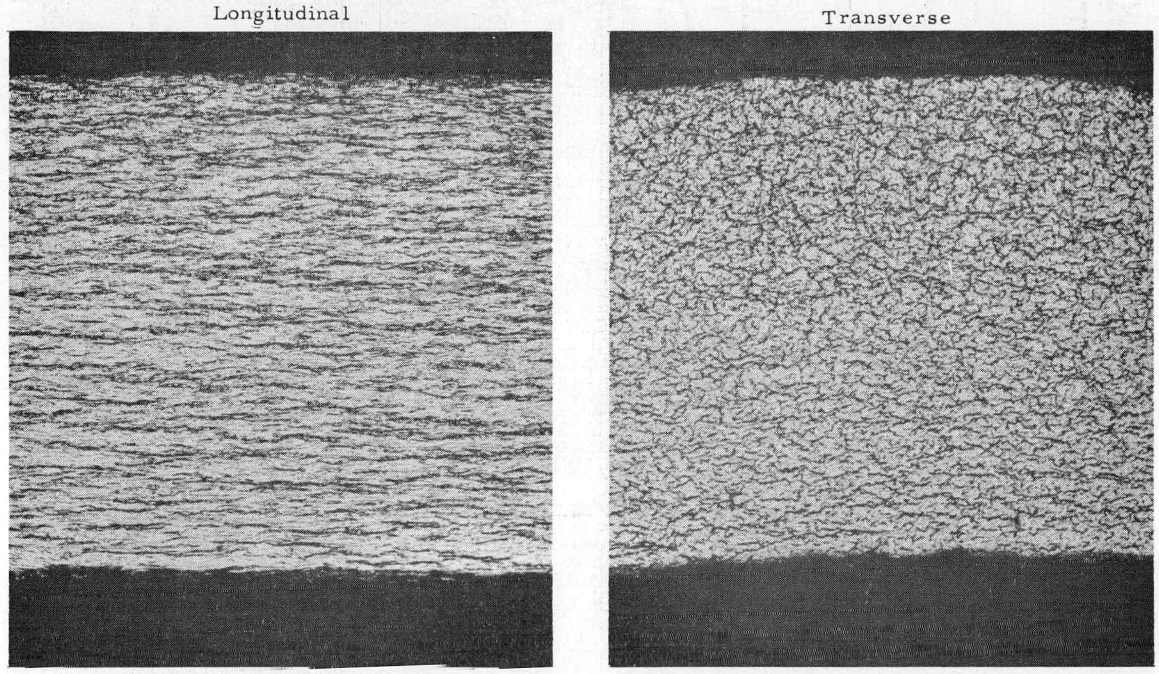
PM365 Lactic-HNO_3-HF 100X

Figure 4. Effect of Thermal Aging on the Microstructure of Hydrided Zircaloy (hydrogen content ≈ 350 ppm)



Lactic-HNO_3-HF 100X Lactic-HNO_3-HF 100X

Aged 45 Minutes at 800 F Before Tensile Test



Lactic-HNO_3-HF 100X Lactic-HNO_3-HF 100X

Unaged Before Tensile Test

Figure 5. Effect of Time at Temperature on the 800 F Tensile Properties of Zircaloy-4 Containing 450 ppm Hydrogen

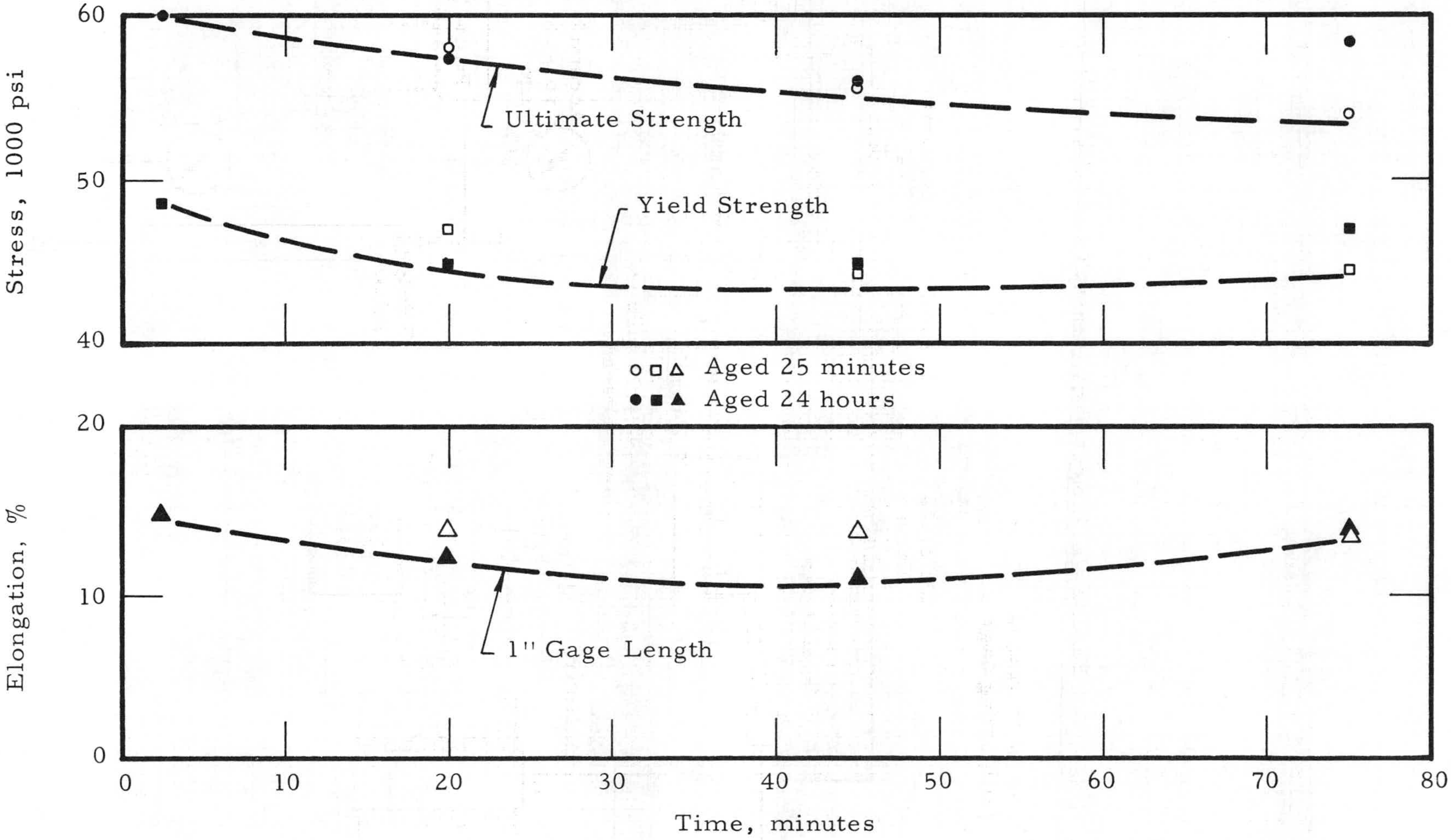


Figure 6. Diagram of Burst-Test Facility

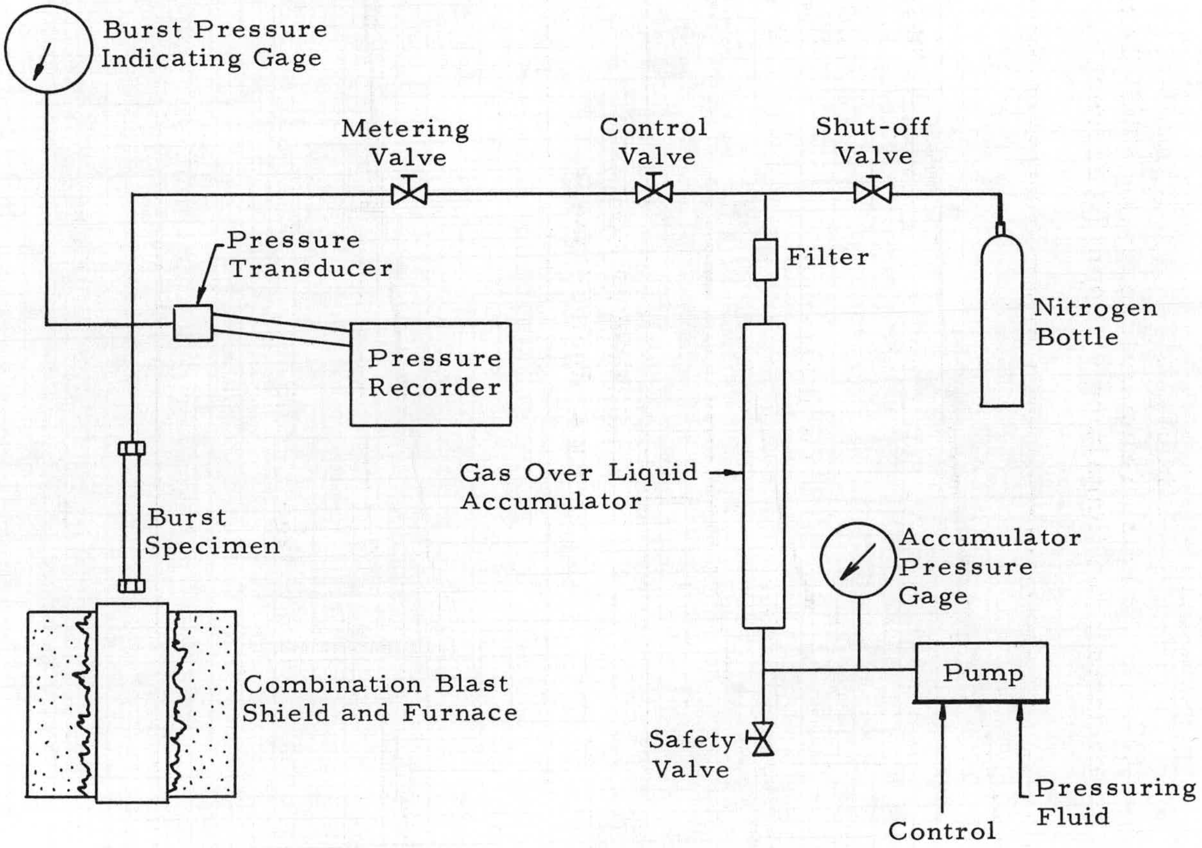


Figure 7. Burst-Test Apparatus (WAS-67-1023)

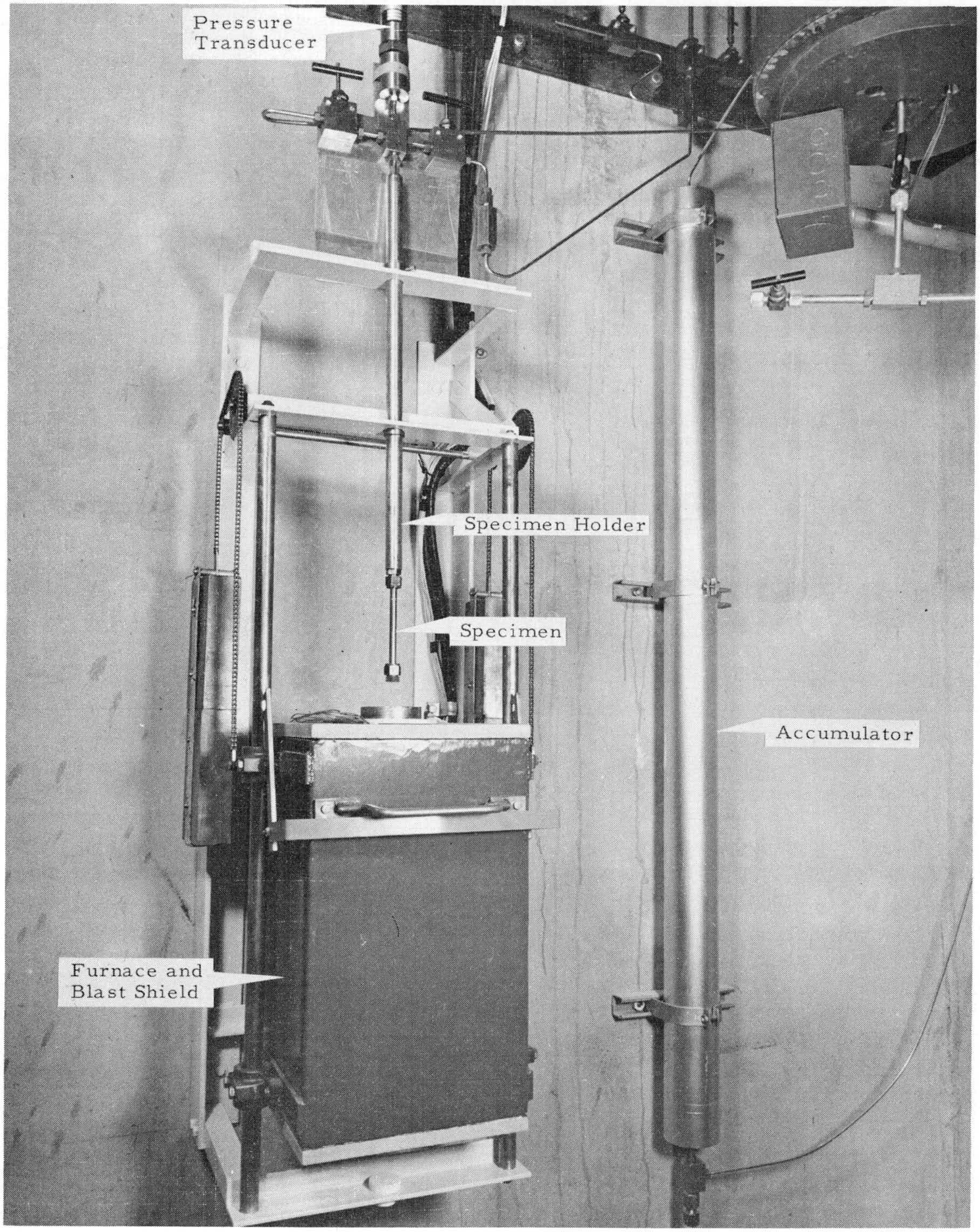
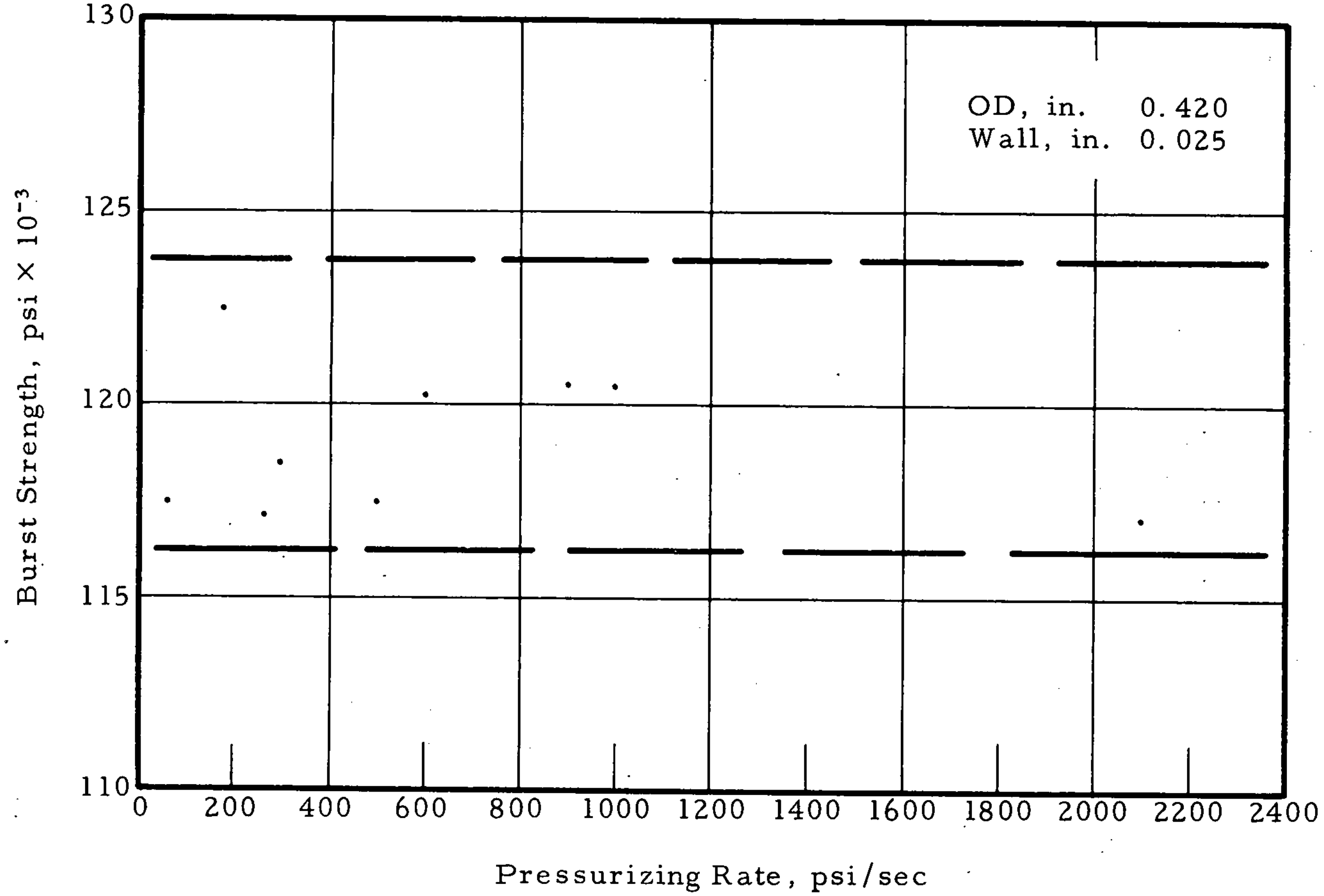


Figure 8. Effect of Pressurizing Rate on Burst Strength of Zircaloy-4 Tubing



4. RESULTS

4.1. Tensile Tests

The tensile strength data for cold-worked Zircaloy-4 containing from 20 (representative of the as-received hydrogen content) to 1000 ppm hydrogen and tested over the range from room temperature to 800 F are shown in Figures 9 through 14 and are summarized in Figure 15. The data represent the average values obtained from testing three specimens at each condition. The range of the data at each test condition is represented by the connected extension bars.

Corresponding tensile elongation data are shown in Figures 16 through 21 and are summarized in Figure 22. The elongation data are presented for three different gage lengths to illustrate better the ductility characteristics of Zircaloy. The spread in the curves indicates the degree of localized deformation. Curves that are closely spaced indicate considerable uniform deformation, while a large spread in the curves with reduced gage lengths indicates localized deformation.

The variations in the tensile and yield strength data for the cold-worked material are illustrated in Figure 15. These represent the extreme values for all hydrogen concentrations plotted as a function of test temperature. The extreme variations in the data, compared to the mean value for as-received cold-worked specimens, are within approximately 10% at any test temperature.

The maximum variations in the total elongation data measured over a 2-inch gage length are plotted in Figure 22. The curves for the mean values of the as-received material and the material containing 1000 ppm hydrogen are shown for comparison. At temperatures above about 300 F, the increase in hydrogen content causes a reduction in total elongation to approximately 60% of the value for as-received material. Below 300 F the elongation decreases with decreasing temperature, and at room temperature elongation of the hydrided material with 1000 ppm hydrogen is approximately one third of the value of the as-received material.

The tensile strength data for the annealed Zircaloy-4 are shown in Figures 23 through 28 and are summarized in Figure 29. These data are for hydrogen concentrations of 20 through 1000 ppm and for test temperatures from 70 through 800 F. The corresponding tensile elongation data are shown in Figures 30 through 35 and are summarized in Figure 36. The elongation data are presented for three different gage lengths to illustrate better the ductility characteristics of the material. (Data were also shown for three gage lengths of cold-worked specimens.)

The maximum variations in the tensile and yield strength data for the annealed material are plotted in Figure 29; these represent the extreme strength values for all hydrogen concentrations of the annealed material. The mean value of the annealed as-received material is shown for comparison. The extreme variations of the hydrided material are within 15 to 20% of the as-received material at all test temperatures.

The maximum variations in the total elongation data for the annealed material, measured over a 2-inch gage length, are plotted in Figure 36. The curves for the mean values of the as-received material and for the material containing 1000 ppm hydrogen are shown for comparison. The effect of hydrogen content on the ductility of the annealed Zircaloy is most severe at temperatures below about 200 F and above 500 F. At temperatures below 200 F, a hydrogen concentration of 1000 ppm reduces the elongation by approximately half. At temperatures above 500 F, the same hydrogen concentration reduces the elongation by roughly one third.

4.2. Burst Tests

The room-temperature burst strengths of both annealed and cold-worked material are plotted in Figure 37. The cold-worked material exhibits a sharp reduction in burst strength at hydrogen concentrations of more than 250 ppm. The total reduction in burst strength associated with the increase in hydrogen concentration from 20 to 1000 ppm is 30,000 psi, which represents a 25% loss of burst strength.

The annealed material exhibited a gradual reduction in burst strength with increased hydrogen concentration. The total reduction in burst-strength properties of the annealed material was 16,000 psi, or about an 18% reduction in the burst strength of material containing 20 ppm hydrogen.

Representative burst specimens after testing are shown in Figures 38 and 39. There is little apparent difference between the fracture modes of the cold-worked material and those of the annealed material. Above 150 ppm hydrogen, both materials fractured into a large number of pieces and, if any difference exists, the annealed material fractured into more, relatively smaller pieces.

4.3. Metallographic Examinations

The as-hydrided annealed and cold-worked material was examined metallographically to determine the uniformity and orientation of the precipitated hydrides. Representative photomicrographs of the different materials are shown in Figure 40. The hydride is very uniformly distributed throughout the material for all hydrogen concentrations.

The annealed material exhibits a more random orientation of hydrides than does the cold-worked material. This material also has a uniform distribution of hydrides throughout its thickness. The specimens containing hydrogen concentrations of 500 ppm and above appear to have a slight hydride concentration at the surface which was not apparent during visual examination of the specimens before testing.

Representative photomicrographs of the annealed material after testing are shown in Figure 41. There is no apparent change in the structure of the material. The higher test temperatures caused an apparent redistribution and agglomeration of hydrogen in specimens containing more than 250 ppm hydrogen. The cold-worked material is shown in Figure 42. The increased test temperature appeared to disperse the precipitated hydride without affecting the orientation.

Typical fractures of the burst specimens are shown in Figure 43. The precipitated hydride does not appear to be related to the fracture mode, although the hydride platelets would be expected to produce planes of weakness that would influence the fracture path.

Figure 9. Tensile Strength of Cold-Worked Zircaloy-4 Containing 20 ppm Hydrogen

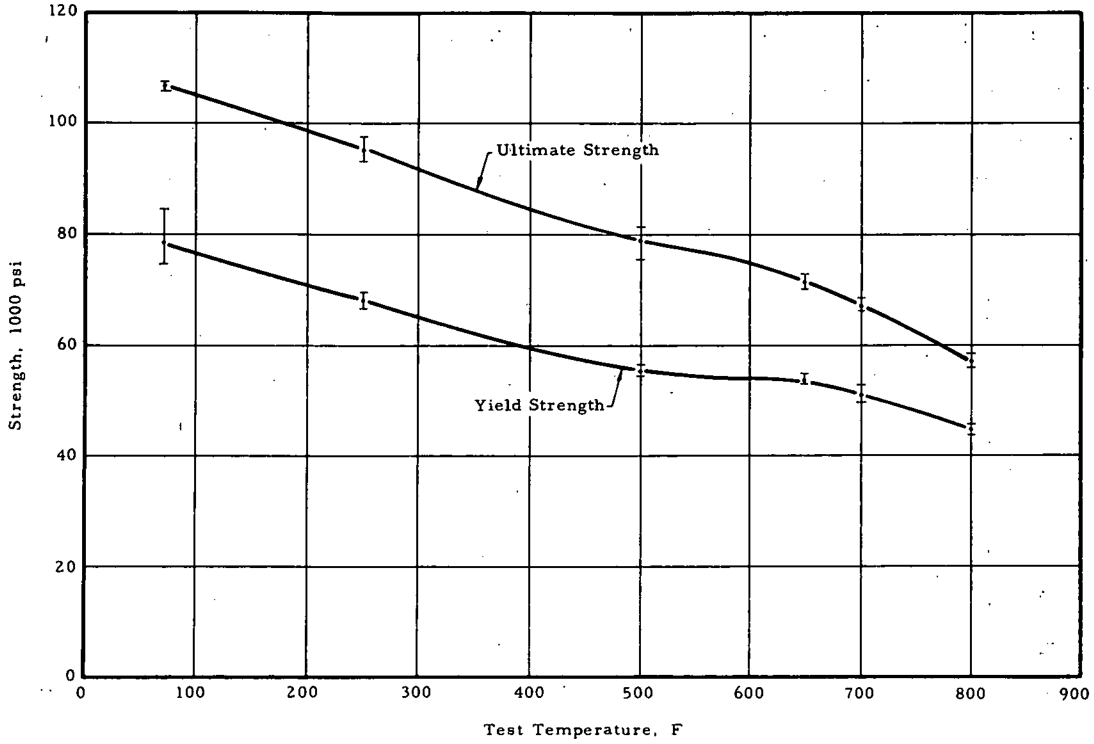


Figure 10. Tensile Strength of Cold-Worked Zircaloy-4 Containing 150 ppm Hydrogen

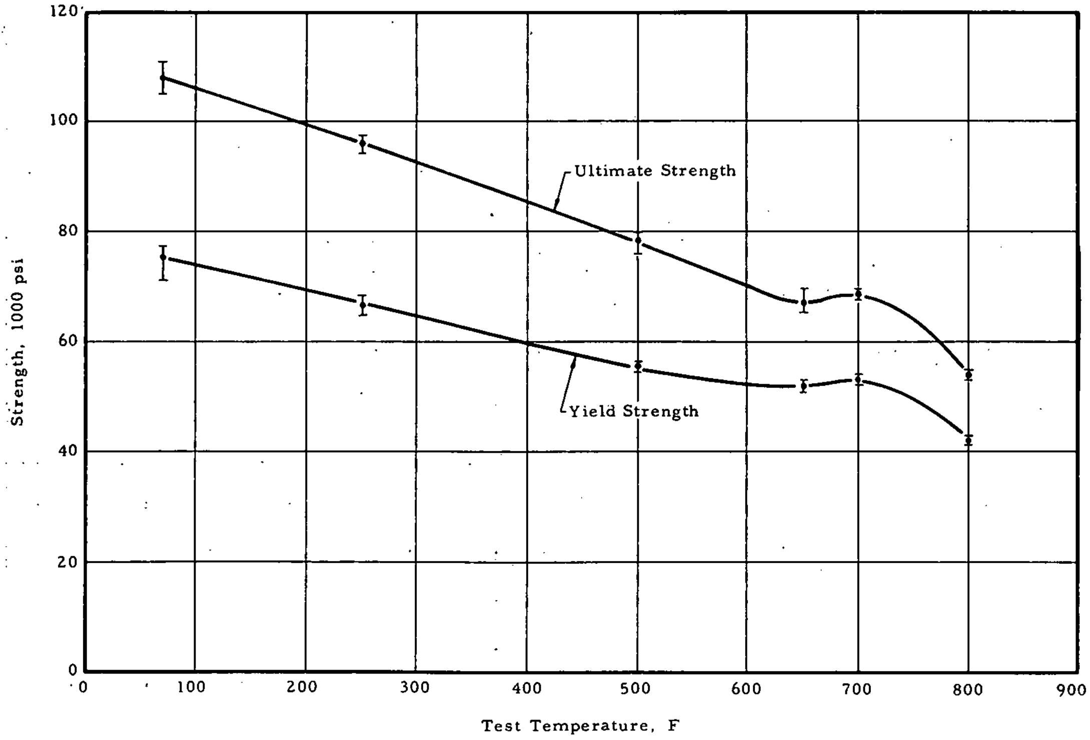


Figure 11. Tensile Strength of Cold-Worked Zircaloy-4 Containing 350 ppm Hydrogen

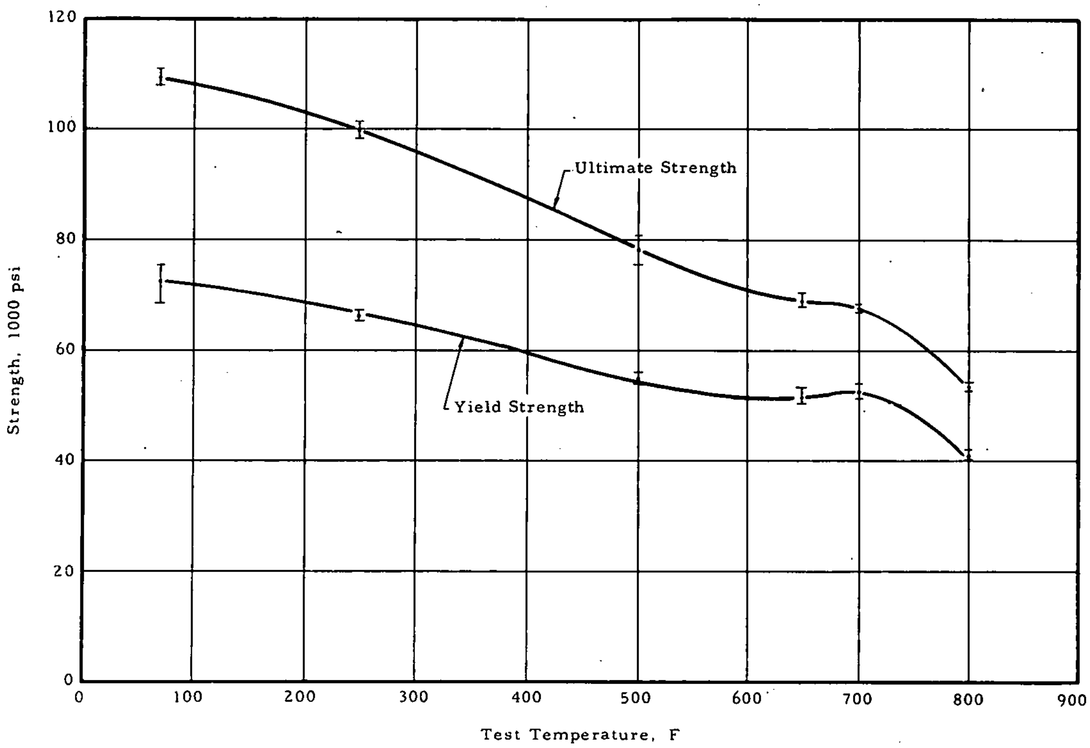


Figure 12. Tensile Strength of Cold-Worked Zircaloy-4 Containing 500 ppm Hydrogen

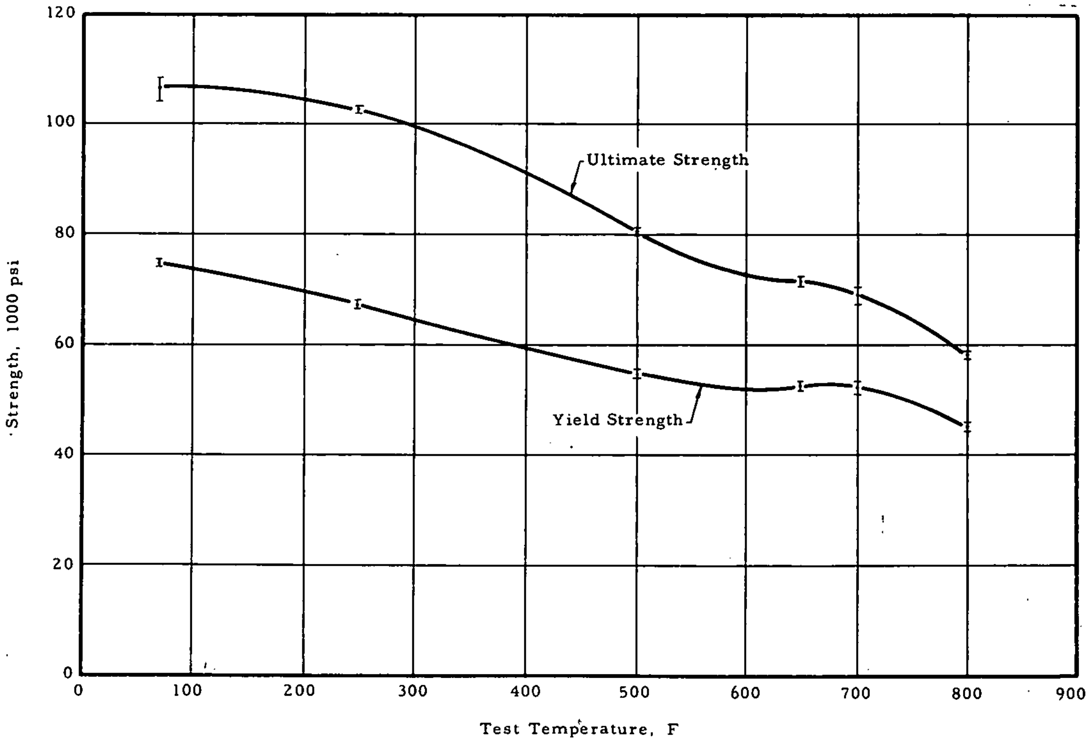


Figure 13. Tensile Strength of Cold-Worked Zircaloy-4 Containing 750 ppm Hydrogen

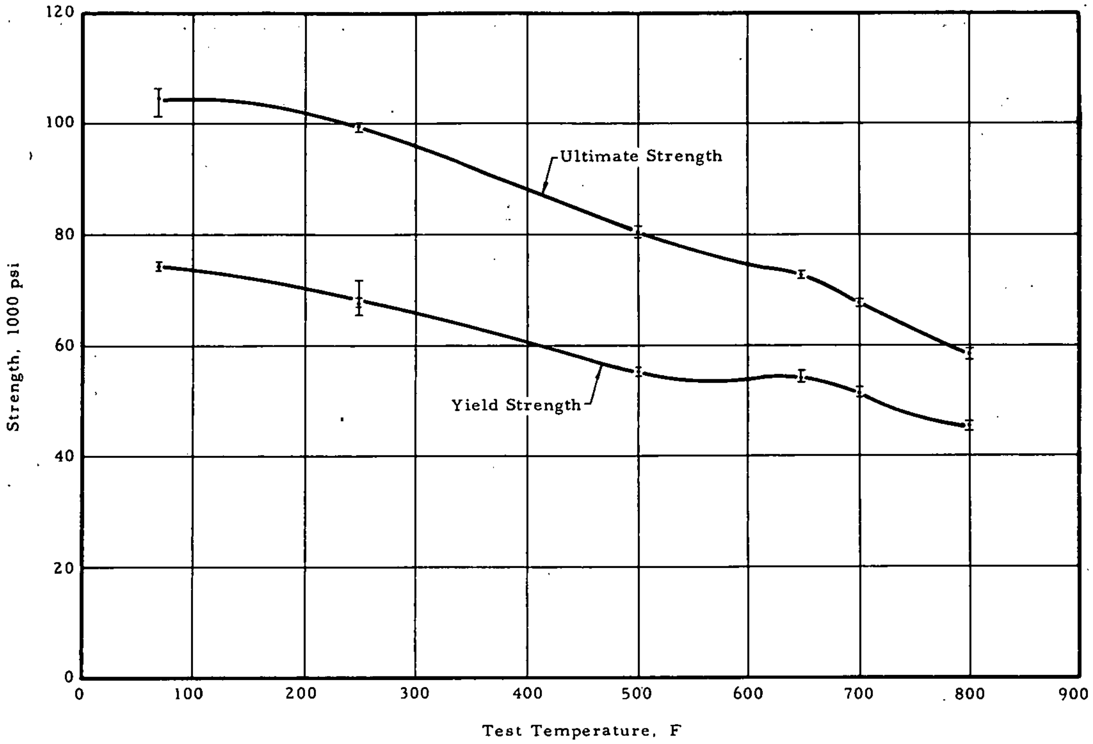


Figure 14. Tensile Strength of Cold-Worked Zircaloy-4 Containing 1000 ppm Hydrogen

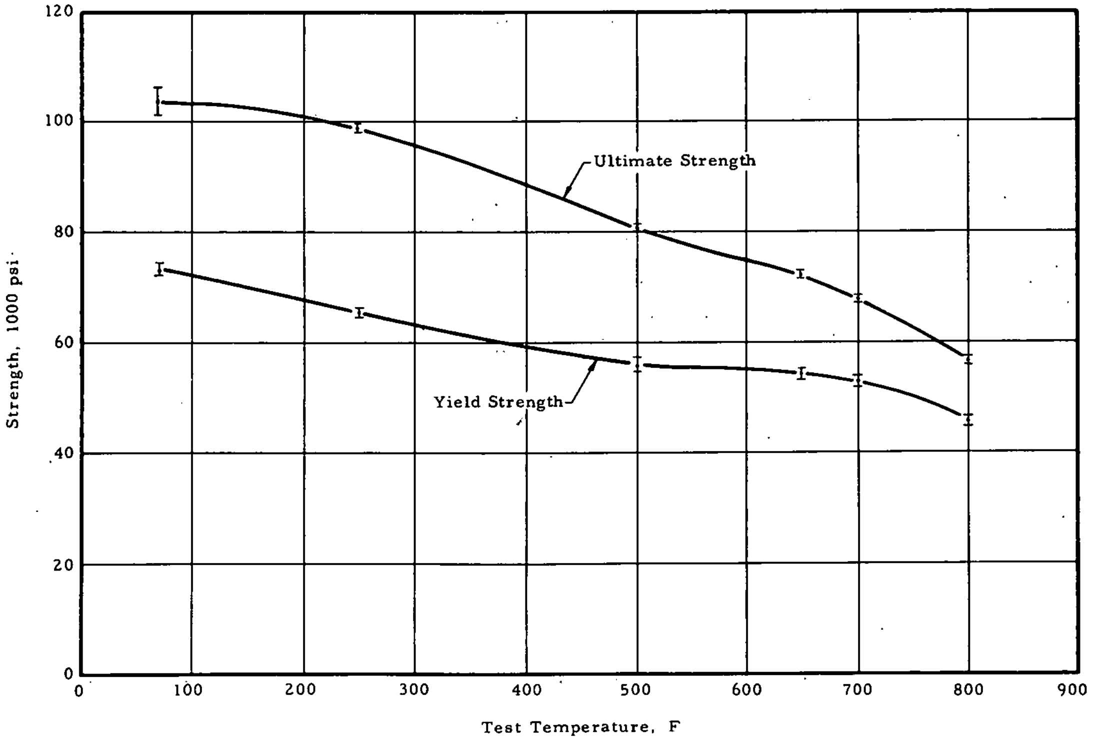


Figure 15. Summary Tensile Strength Bands Encompassing All Data From Cold-Worked Zircaloy-4 Containing 20 to 1000 ppm Hydrogen

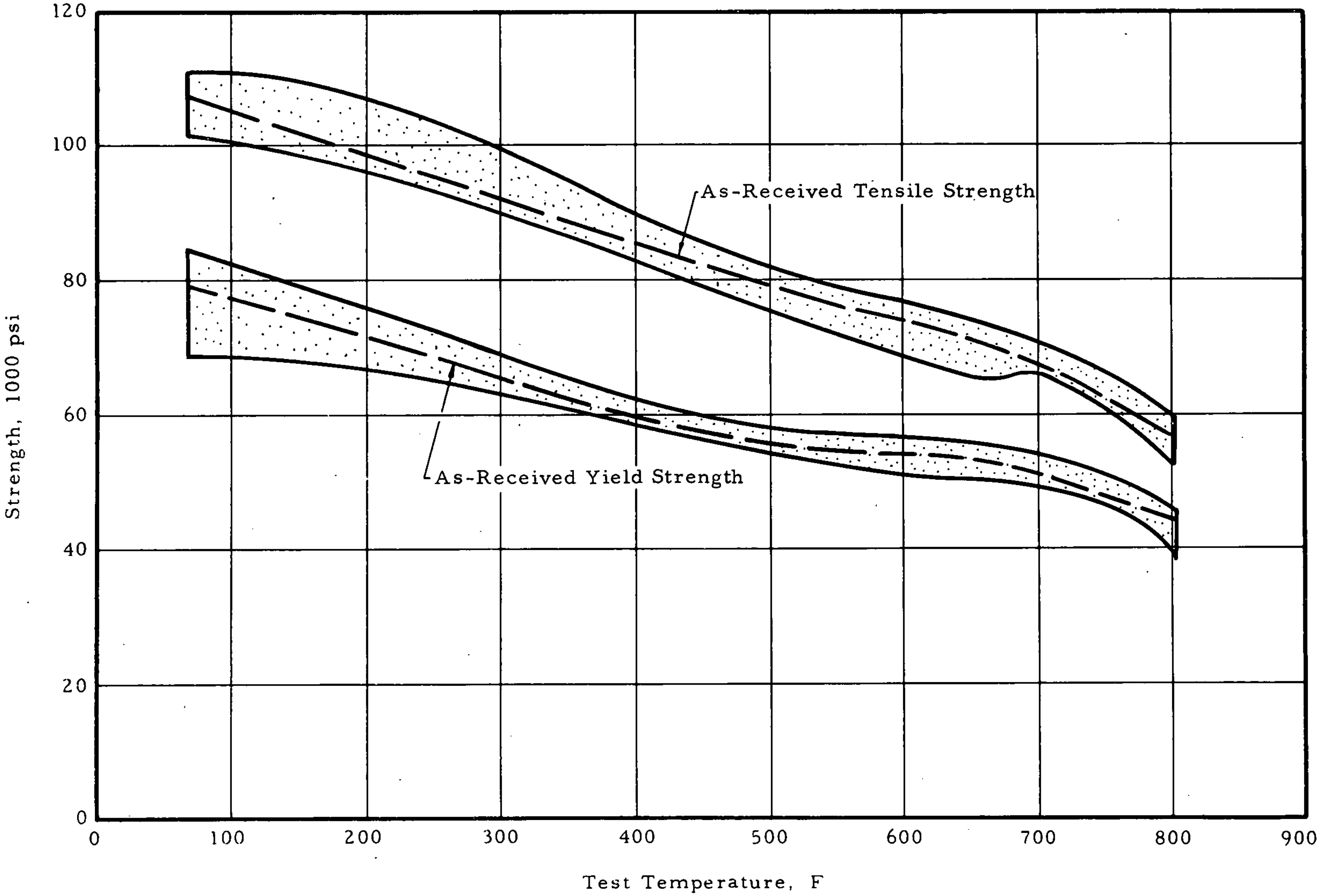


Figure 16. Tensile Elongation of Cold-Worked Zircaloy-4 Containing 20 ppm Hydrogen

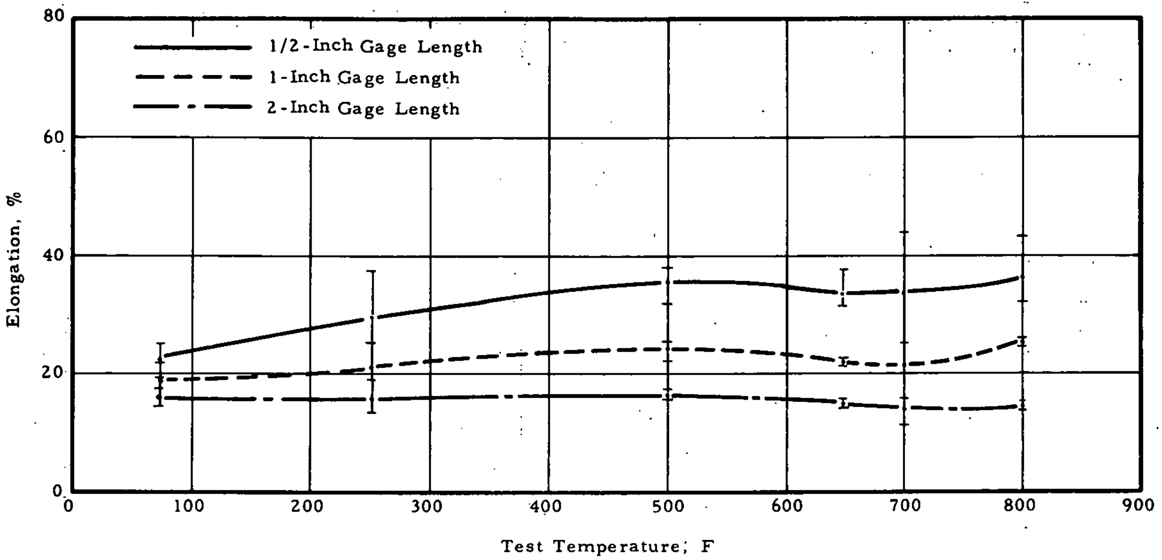


Figure 17. Tensile Elongation of Cold-Worked Zircaloy-4 Containing 150 ppm Hydrogen

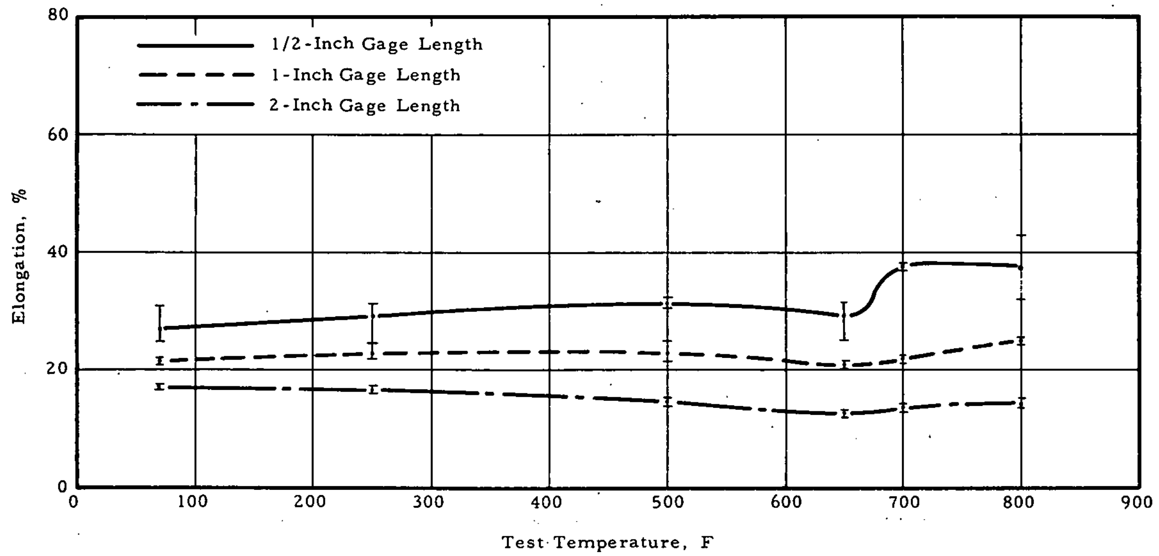


Figure 18. Tensile Elongation of Cold-Worked Zircaloy-4 Containing 350 ppm Hydrogen

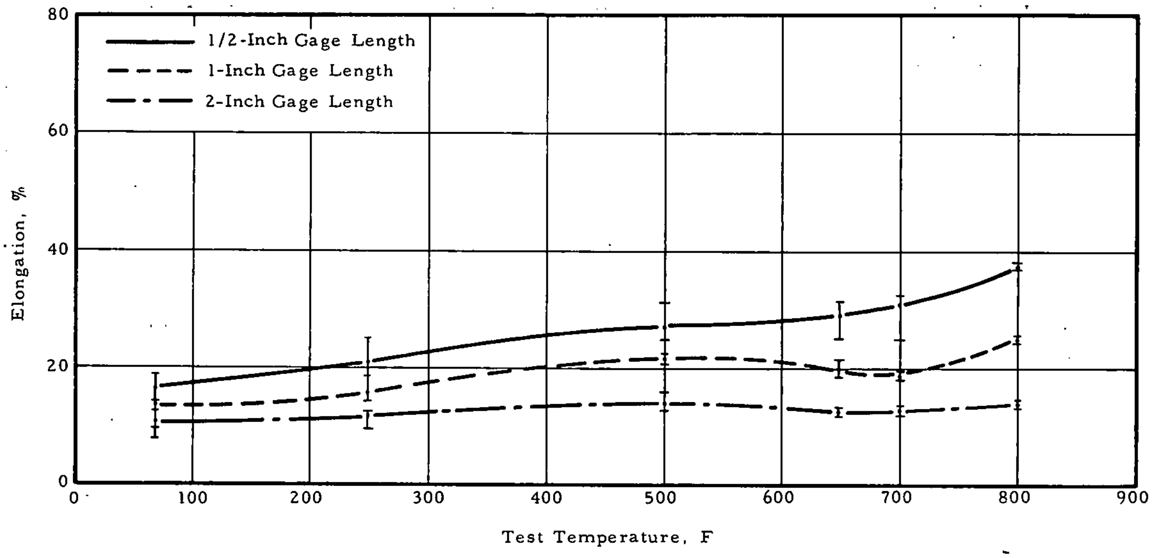


Figure 19. Tensile Elongation of Cold-Worked Zircaloy-4 Containing 500 ppm Hydrogen

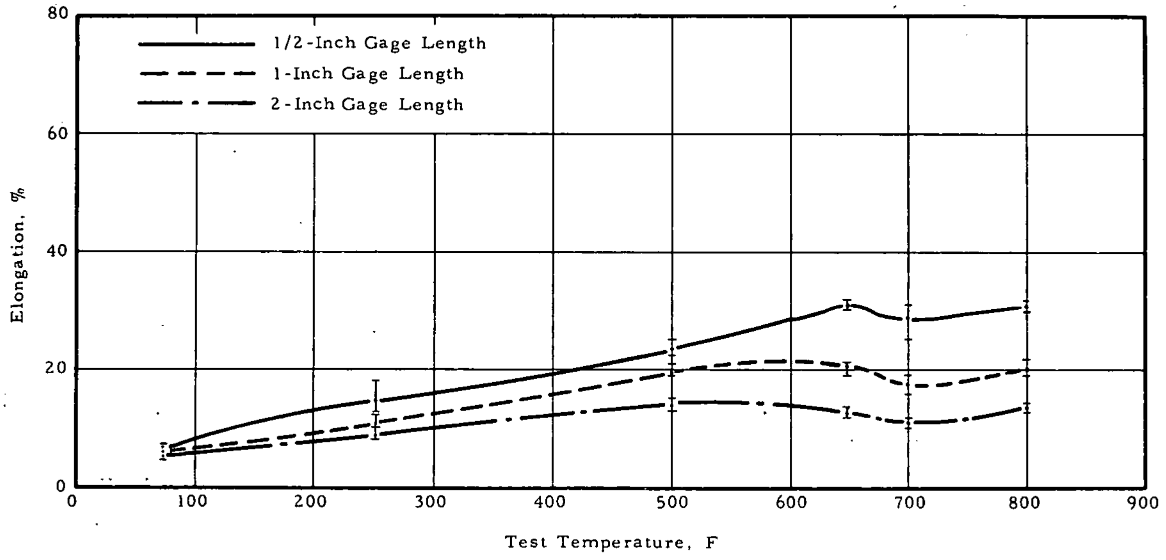


Figure 20. Tensile Elongation of Cold-Worked Zircaloy-4 Containing 750 ppm Hydrogen

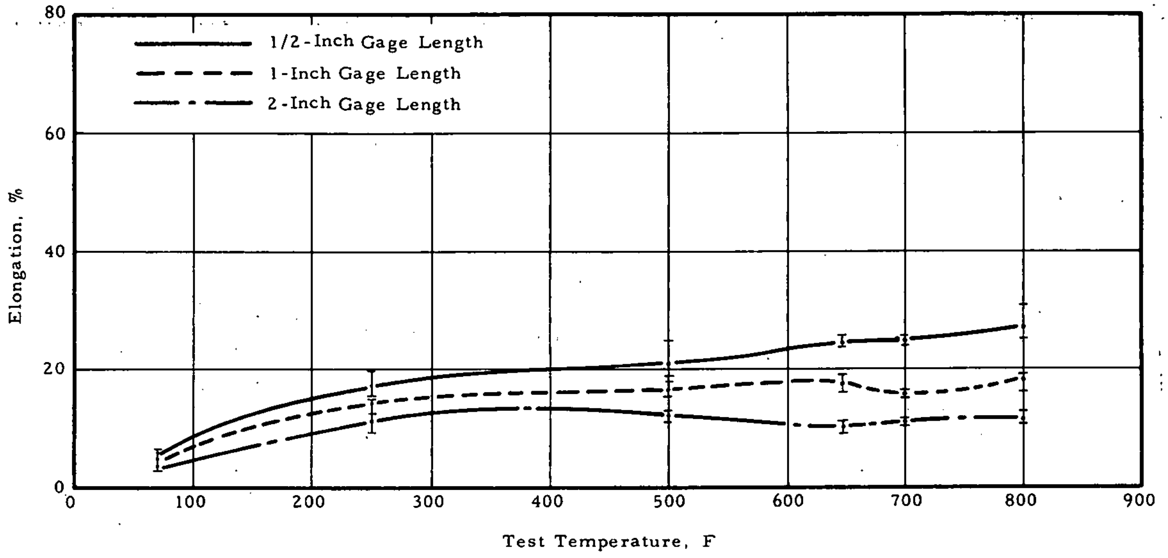


Figure 21. Tensile Elongation of Cold-Worked Zircaloy-4 Containing 1000 ppm Hydrogen.

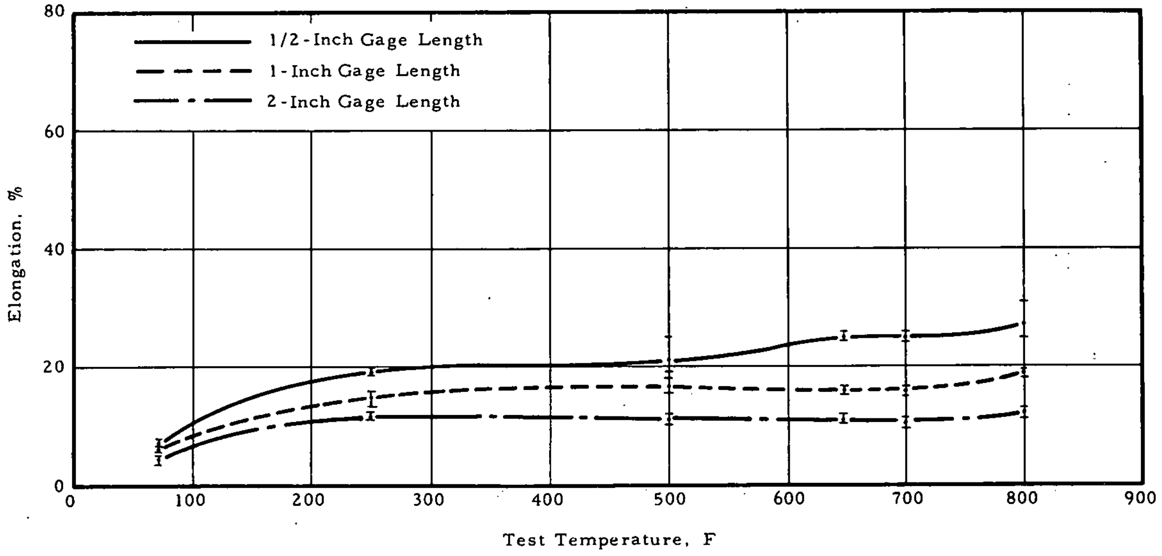


Figure 22. Summary Tensile Elongation Band Encompassing All 2-Inch Gage Length Values for Cold-Worked Zircaloy-4 Containing 20 to 1000 ppm Hydrogen

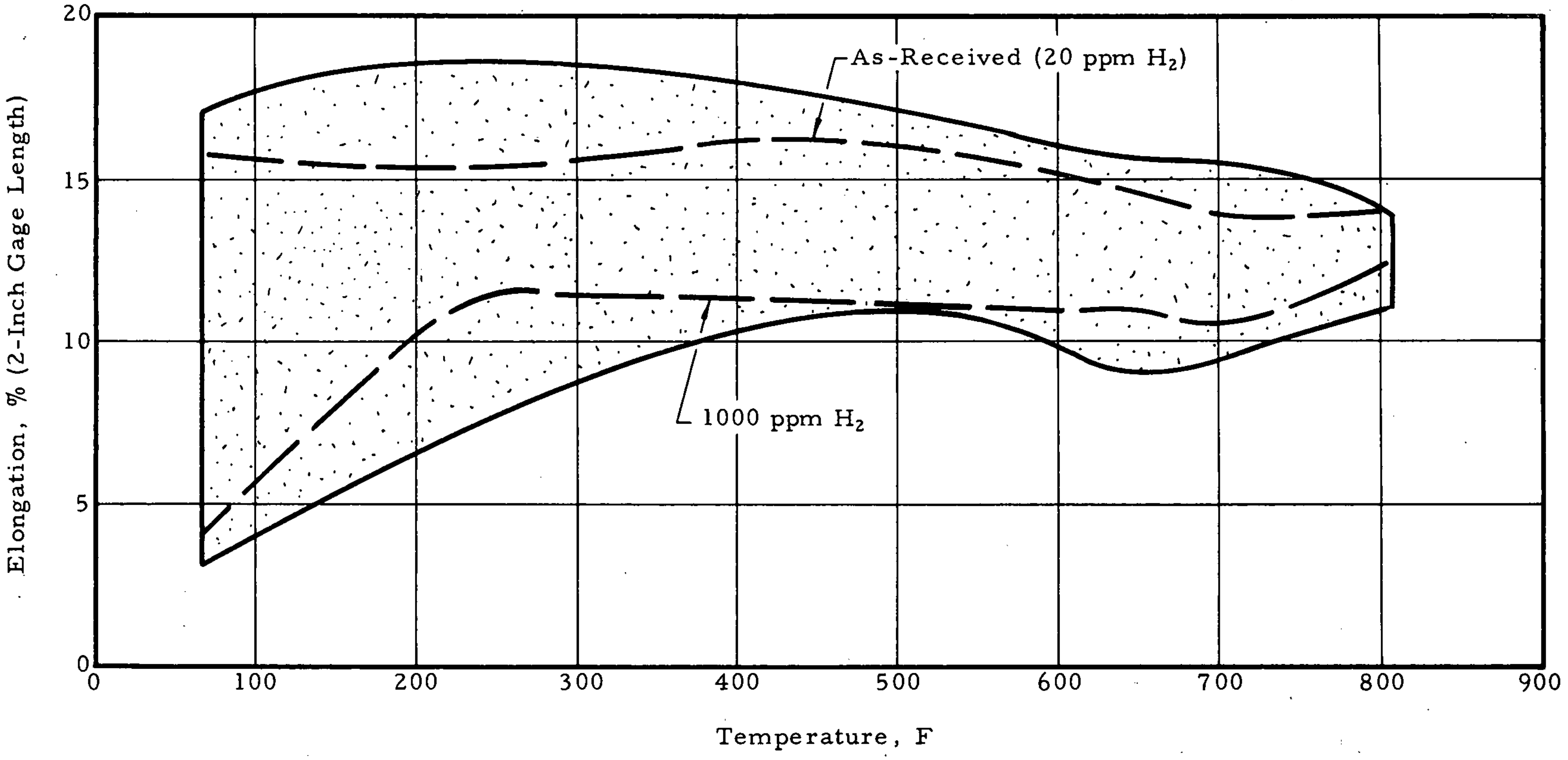


Figure 23. Tensile Strength of Annealed Zircaloy-4 Containing 20 ppm Hydrogen

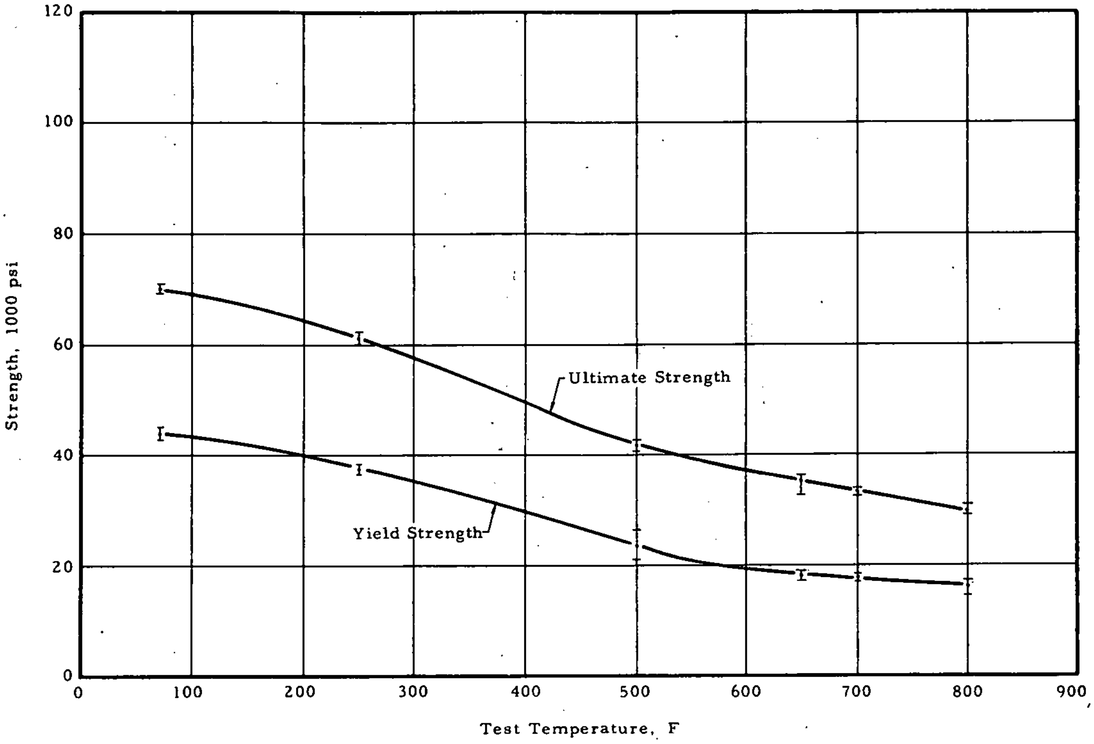


Figure 24. Tensile Strength of Annealed Zircaloy-4 Containing 150 ppm Hydrogen

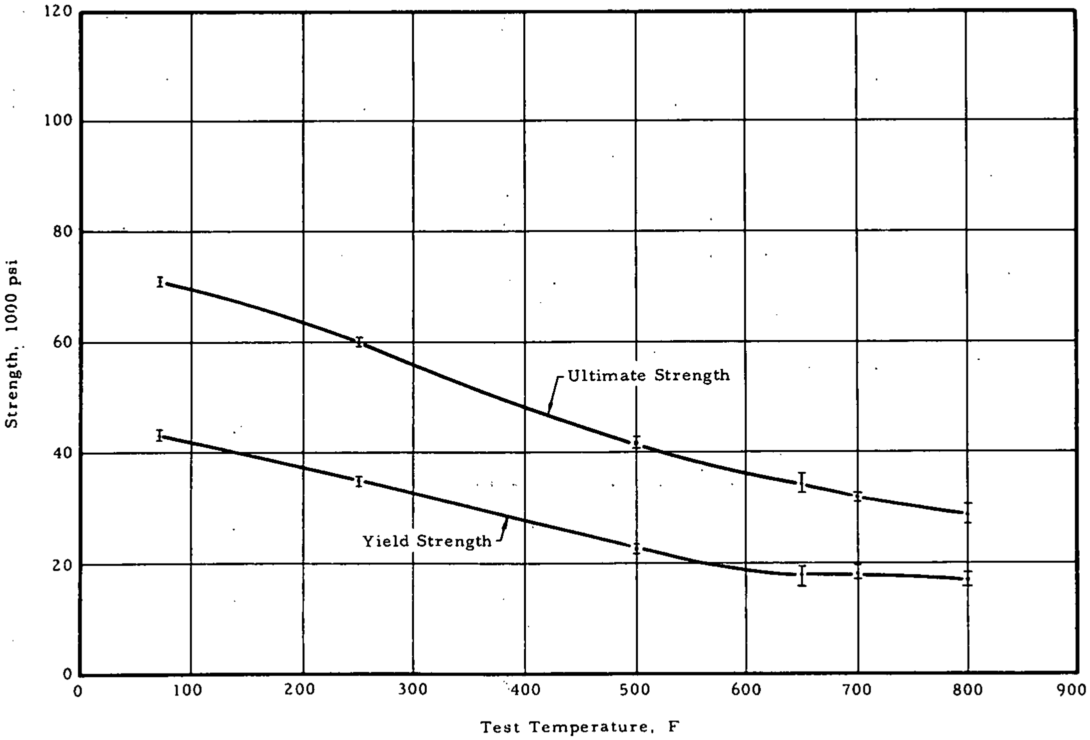


Figure 25. Tensile Strength of Annealed Zircaloy-4 Containing 350 ppm Hydrogen

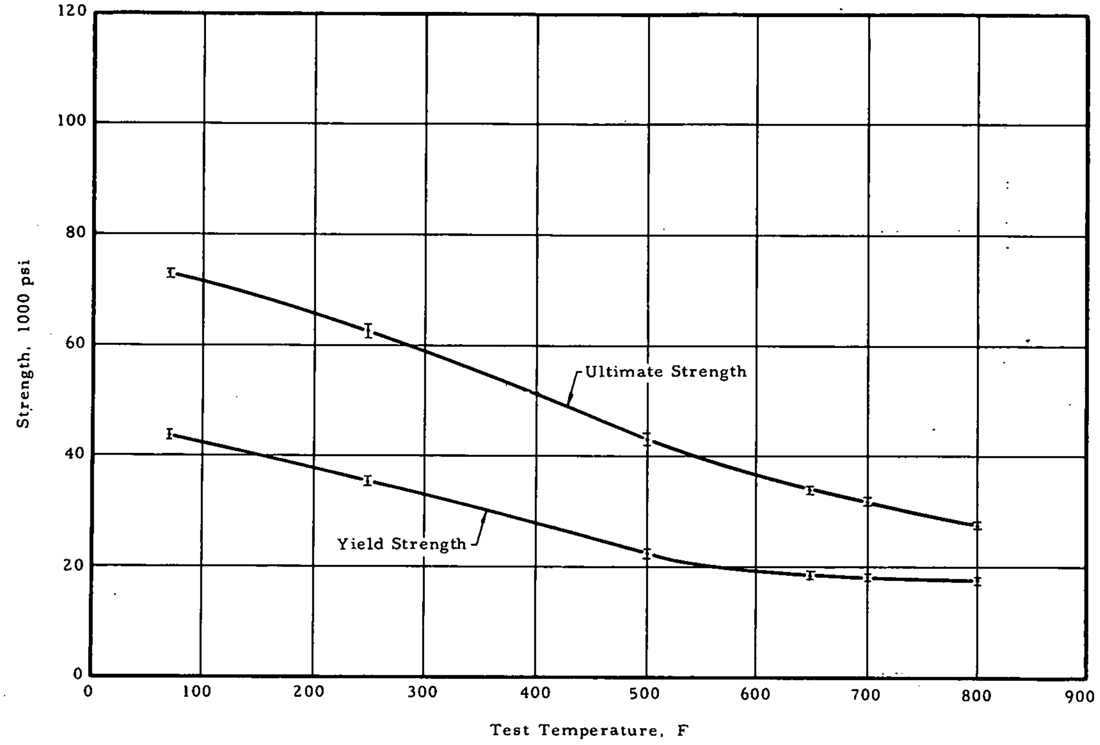


Figure 26. Tensile Strength of Annealed Zircaloy-4 Containing 500 ppm Hydrogen

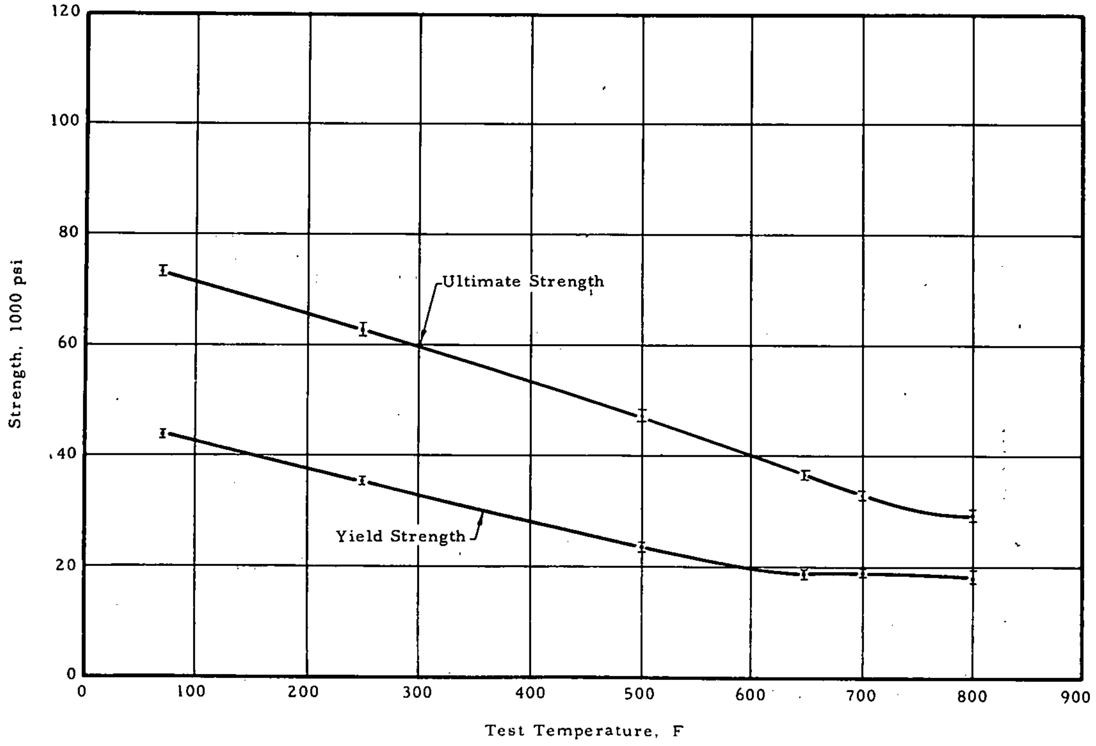


Figure 27. Tensile Strength of Annealed Zircaloy-4 Containing 750 ppm Hydrogen

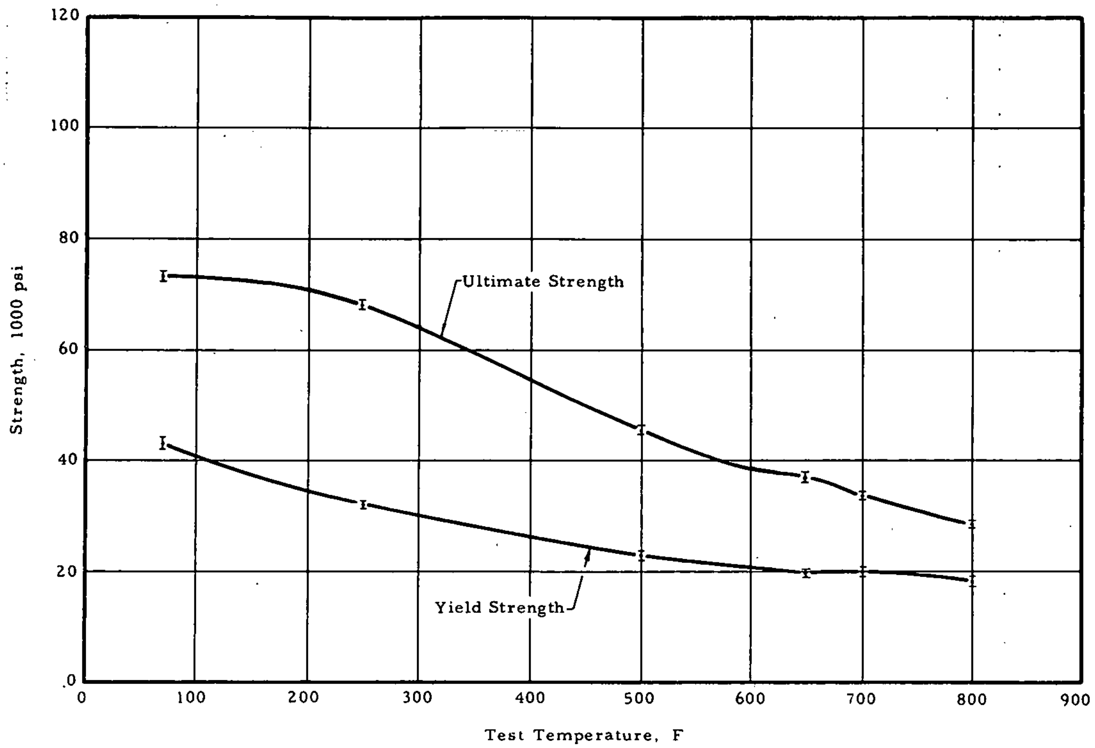


Figure 28. Tensile Strength of Annealed Zircaloy-4 Containing 1000 ppm Hydrogen

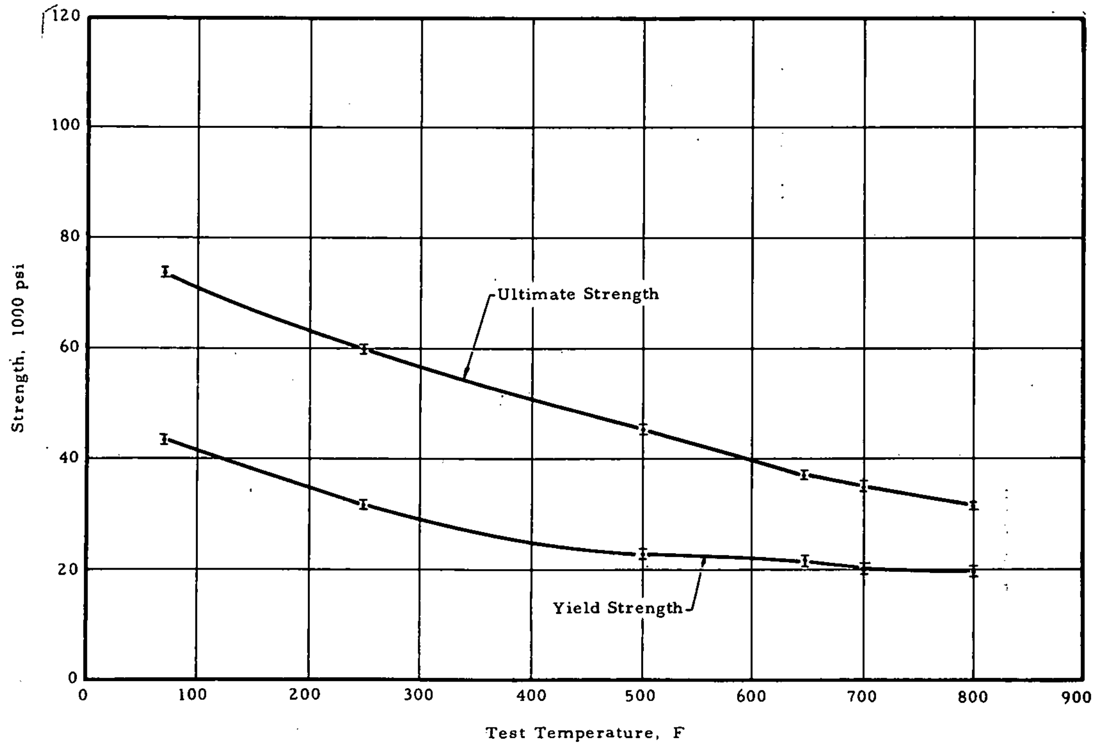


Figure 29. Summary Tensile Strength Bands Encompassing All Data From Annealed Zircaloy-4 Containing 20 to 1000 ppm Hydrogen

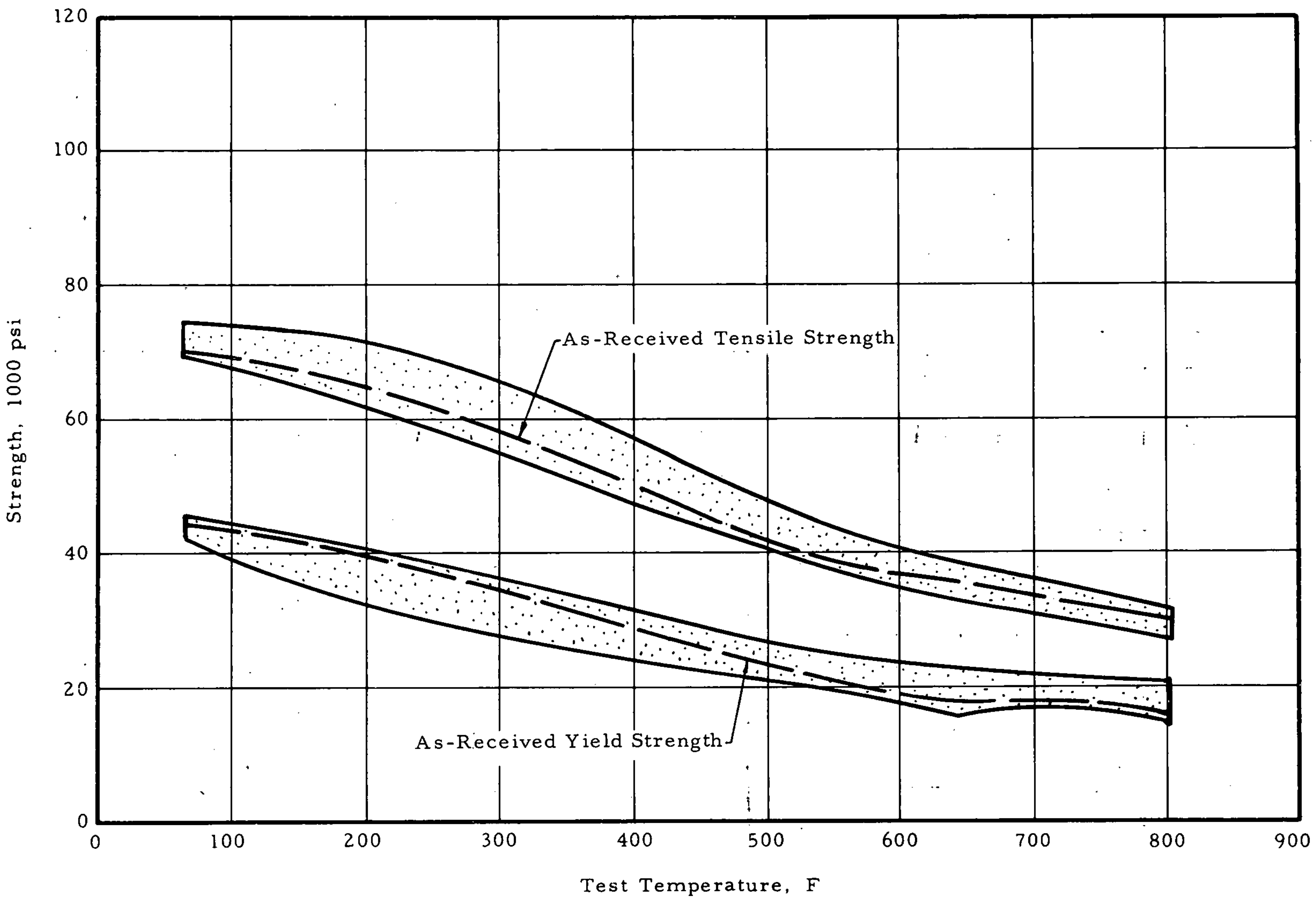


Figure 30. Tensile Elongation of Annealed Zircaloy-4 Containing 20 ppm Hydrogen

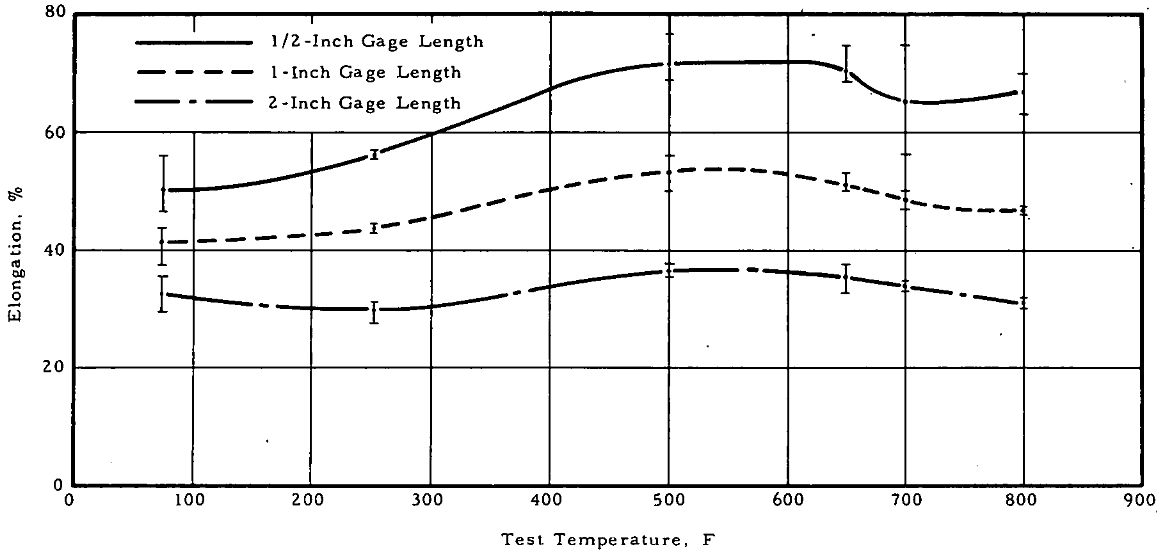


Figure 31. Tensile Elongation of Annealed Zircaloy-4 Containing 150 ppm Hydrogen

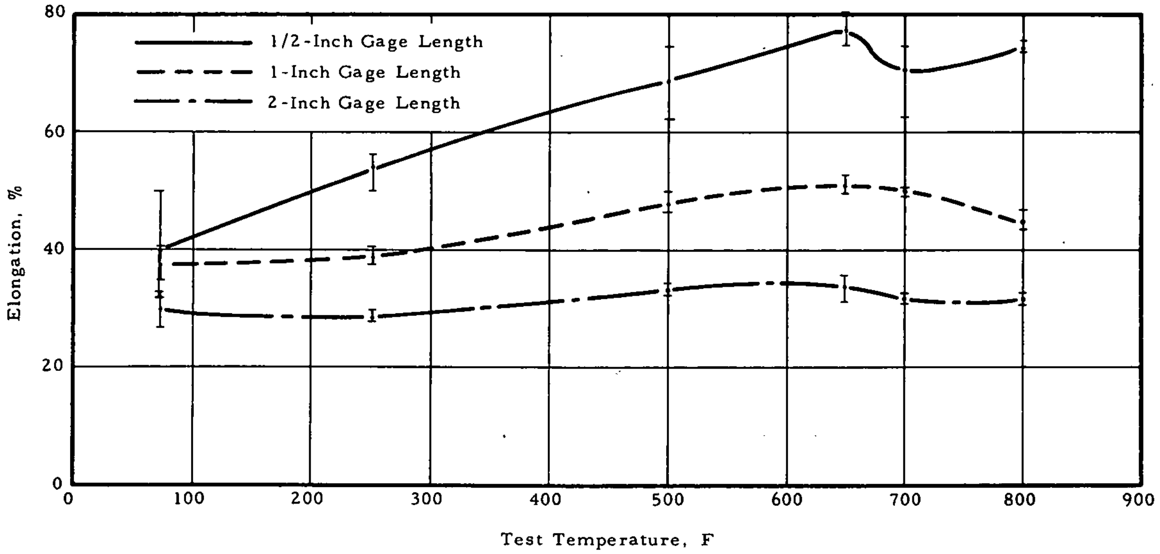


Figure 32. Tensile Elongation of Annealed Zircaloy-4 Containing 350 ppm Hydrogen

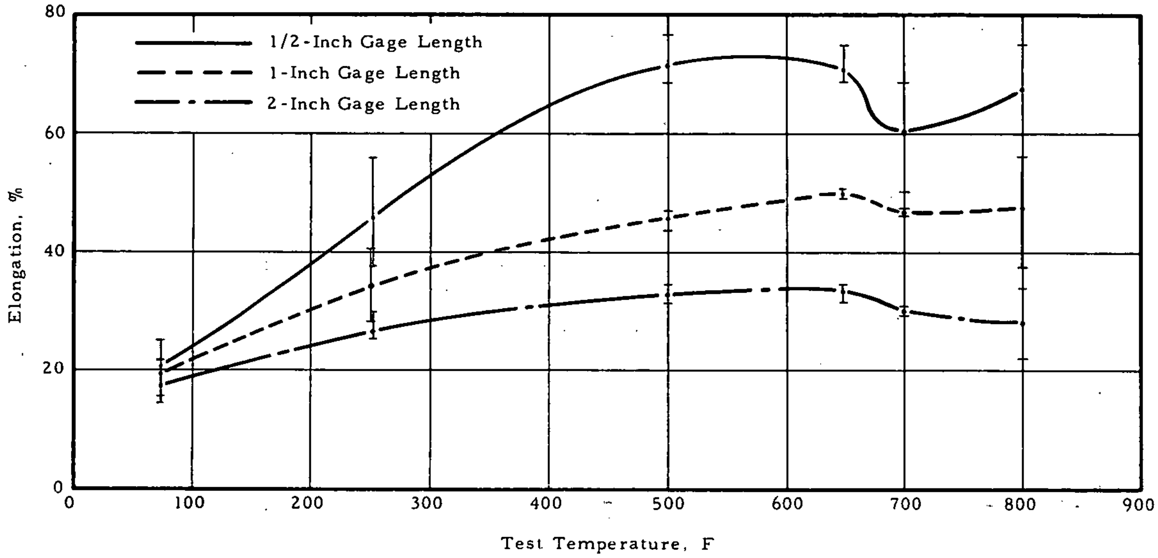


Figure 33. Tensile Elongation of Annealed Zircaloy-4 Containing 500 ppm Hydrogen

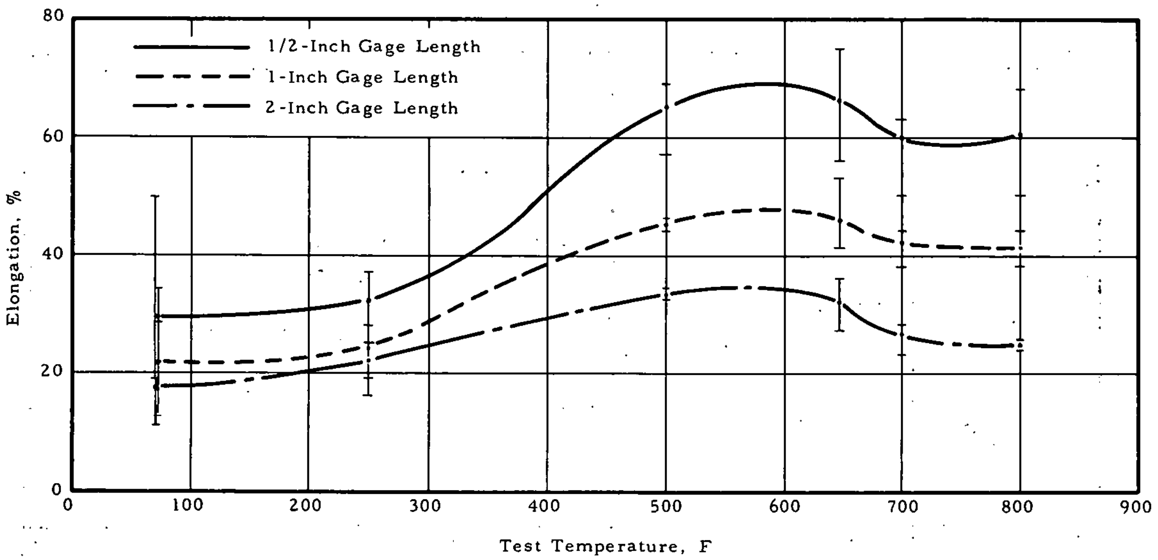


Figure 34. Tensile Elongation of Annealed Zircaloy-4 Containing 750 ppm Hydrogen

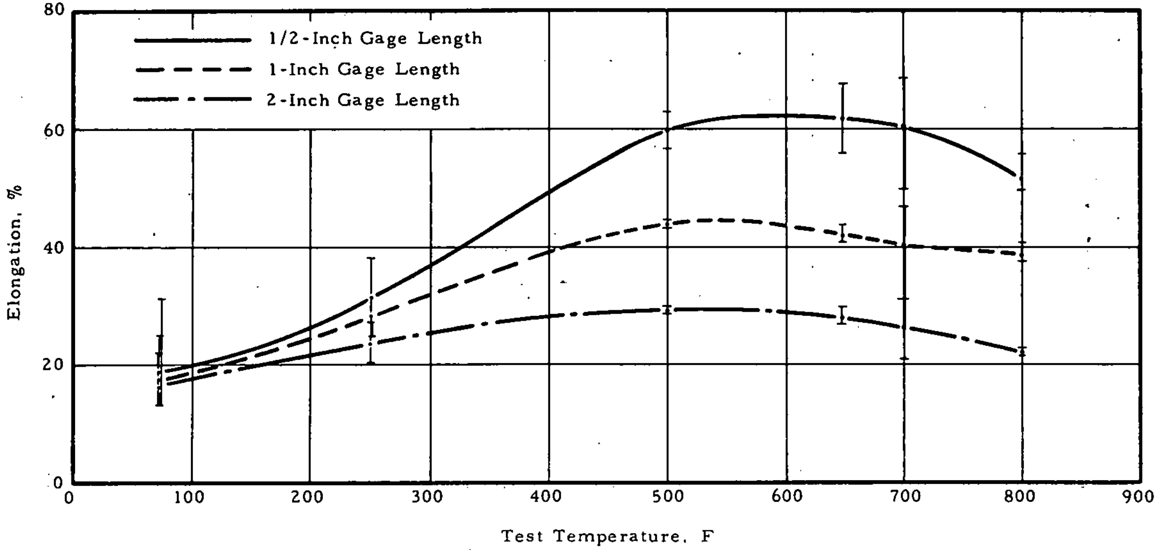


Figure 35. Tensile Elongation of Annealed Zircaloy-4 Containing 1000 ppm Hydrogen

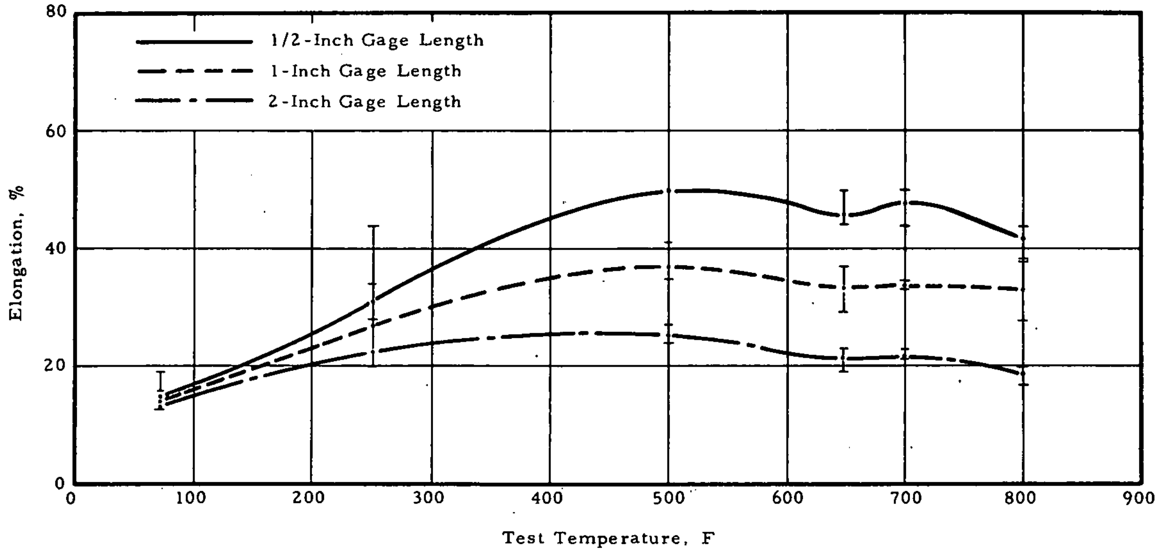


Figure 36. Summary Tensile Elongation Band Encompassing All 2-Inch Gage Length Values for Annealed Zircaloy-4 Containing 20 to 1000 ppm Hydrogen

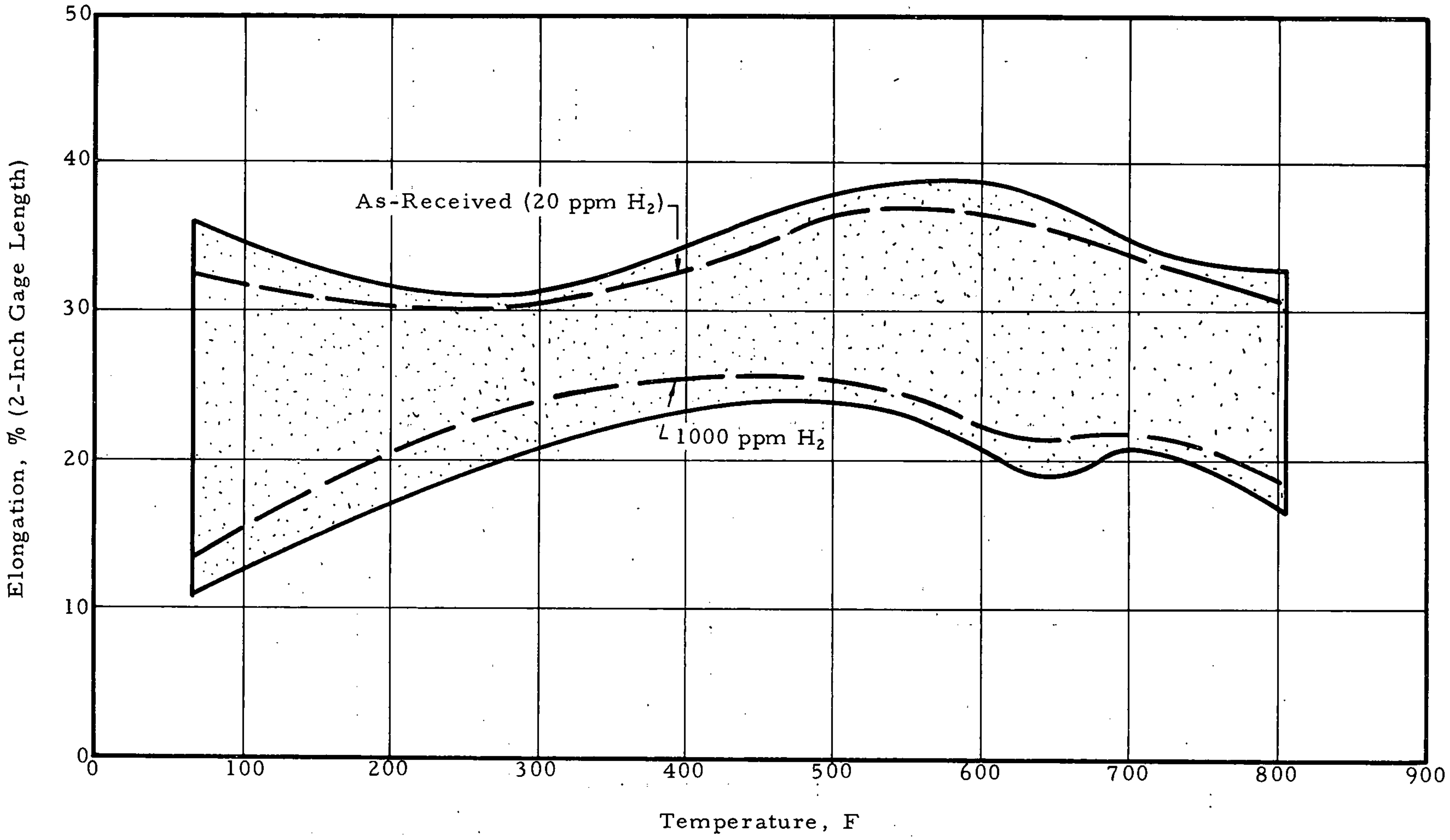


Figure 37. Effect of Hydrogen on the Burst Strength of Cold-Worked and Annealed Zircaloy-4

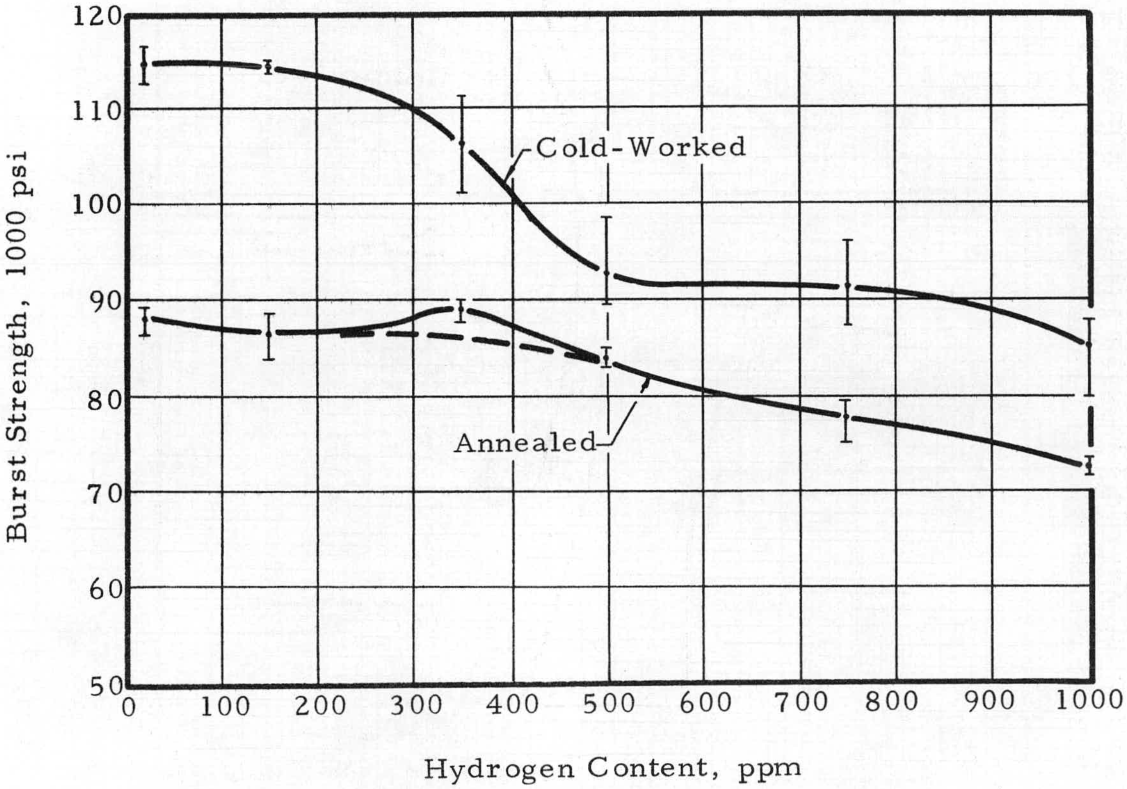
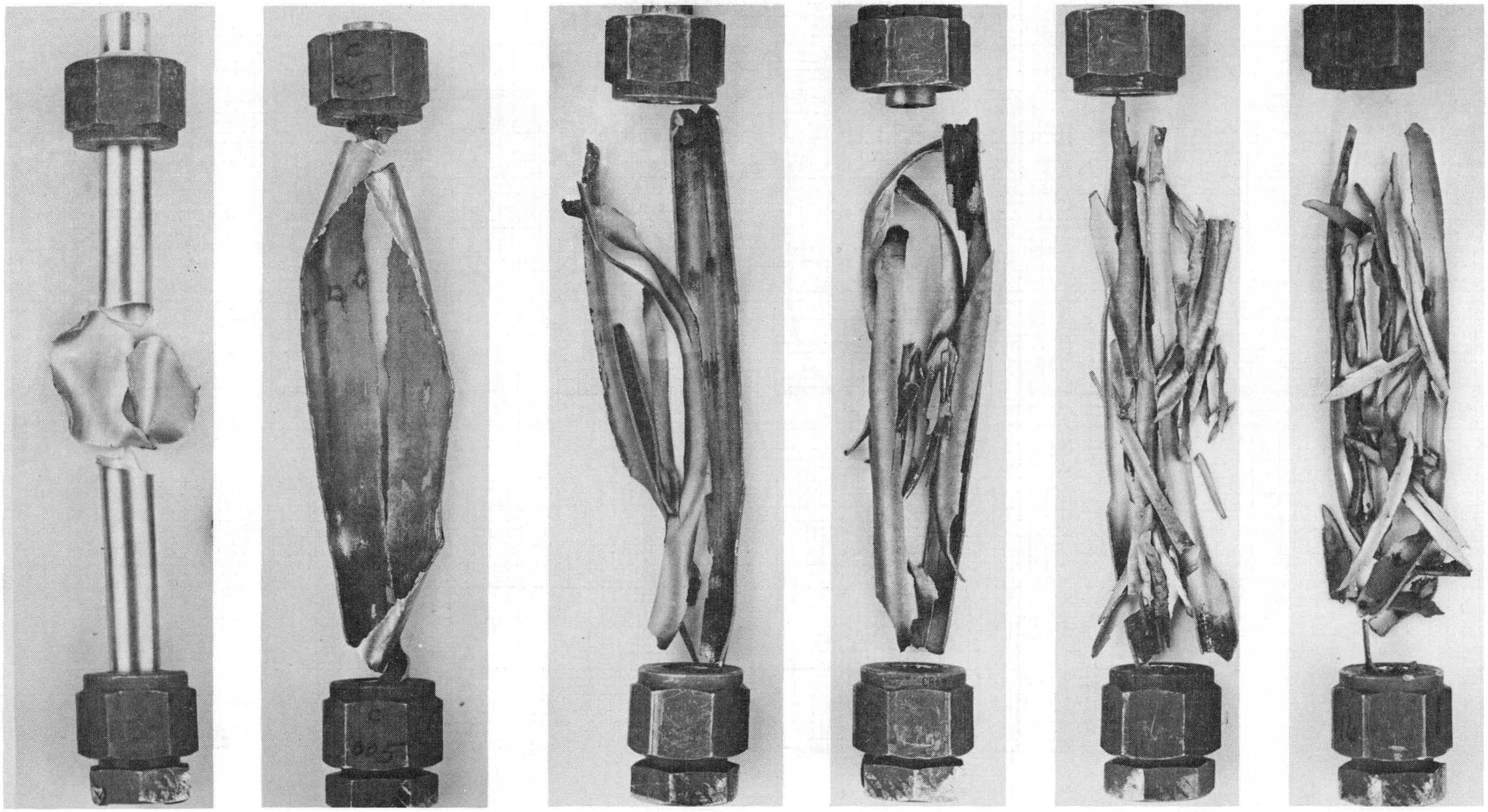
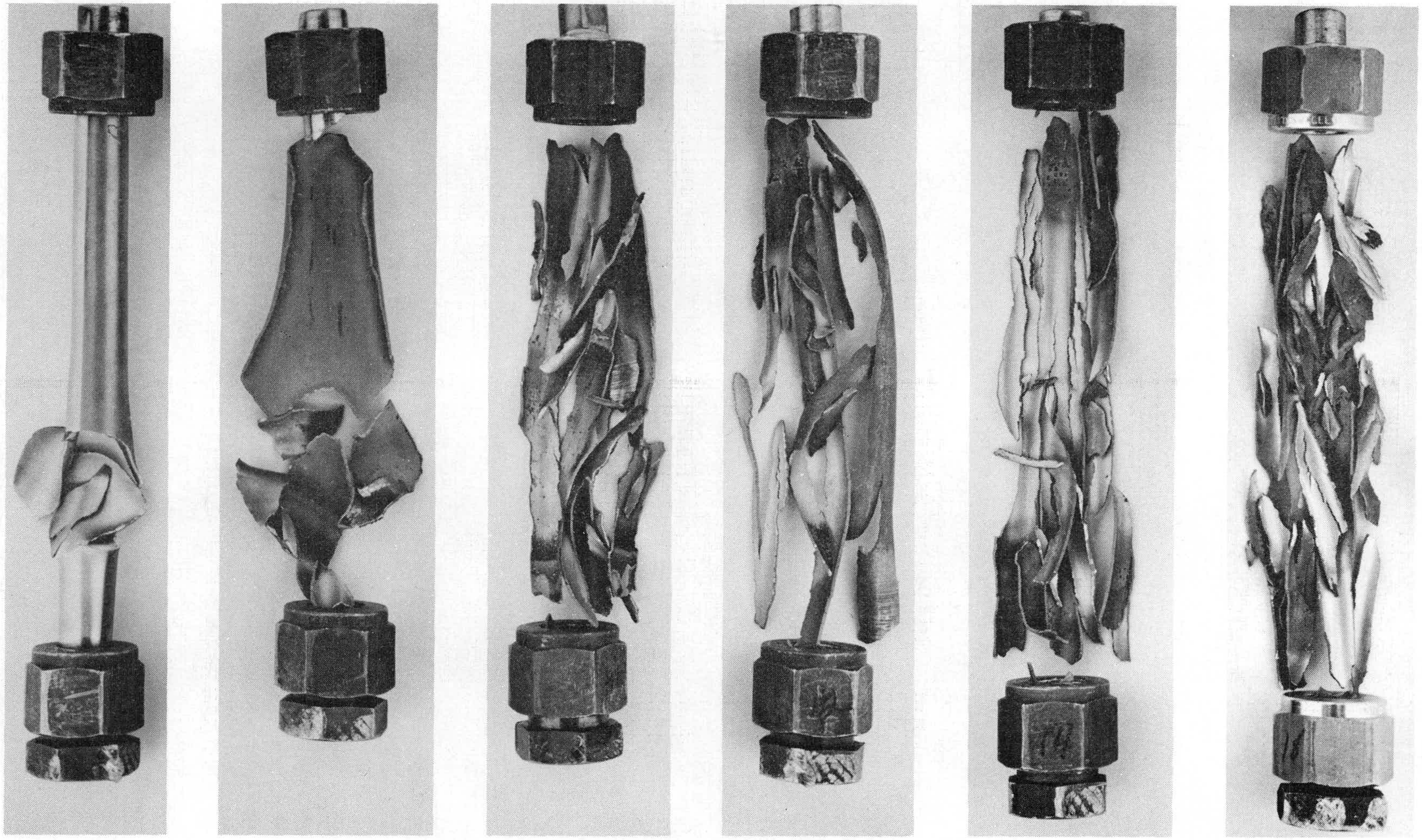


Figure 38. Typical Cold-Worked Zircaloy-4 Burst-Test Specimens Showing Modes of Fracture



20 ppm H_2 150 ppm H_2 350 ppm H_2 500 ppm H_2 750 ppm H_2 1000 ppm H_2

Figure 39. Typical Annealed Zircaloy-4 Burst-Test Specimens Showing Modes of Fracture



20 ppm H_2 150 ppm H_2 350 ppm H_2 500 ppm H_2 750 ppm H_2 1000 ppm H_2

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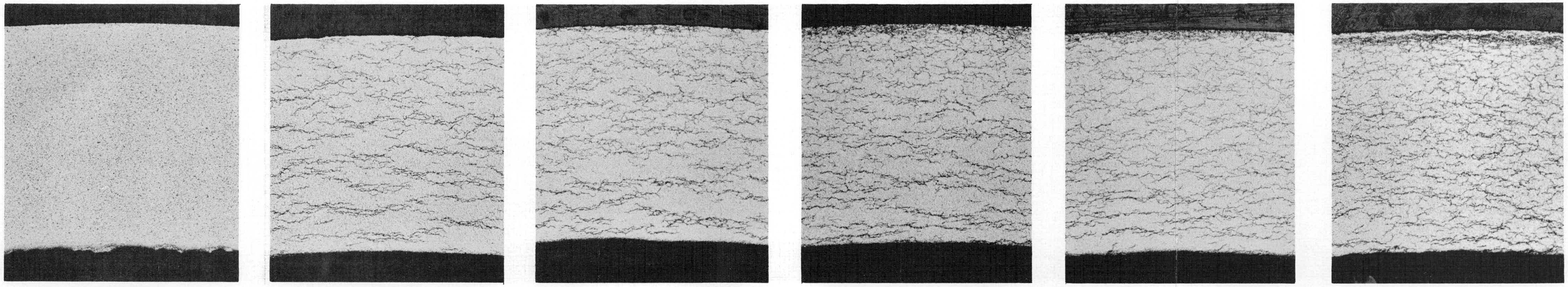
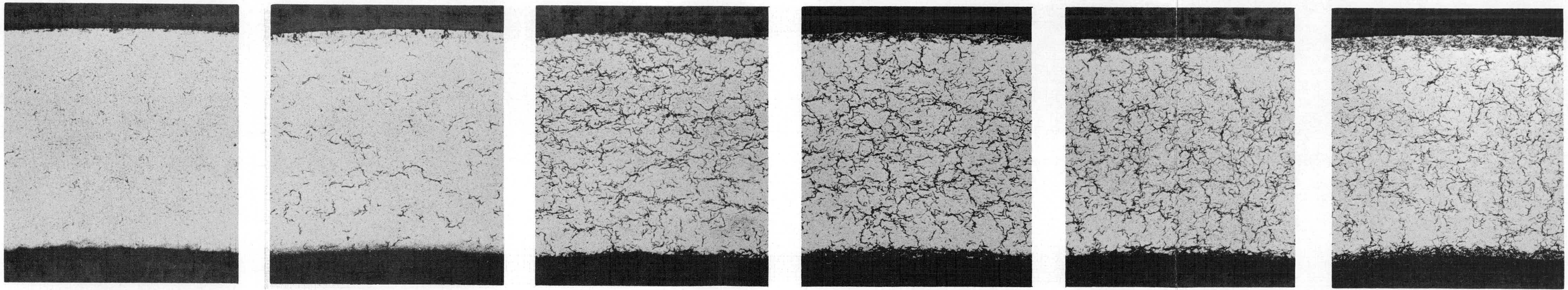
Figure 40. Transverse Sections of Typical Zircaloy-4 Specimens Showing Hydride Distribution and Orientation for Various Hydrogen Concentrations



Cold-Worked, 20 ppm H_2 Cold-Worked, 150 ppm H_2 Cold-Worked, 350 ppm H_2 Cold-Worked, 500 ppm H_2 Cold-Worked, 750 ppm H_2 Cold-Worked, 1000 ppm H_2



Annealed, 20 ppm H_2 Annealed, 150 ppm H_2 Annealed, 350 ppm H_2 Annealed, 500 ppm H_2 Annealed, 750 ppm H_2 Annealed, 1000 ppm H_2

Note: Etch, lactic-HNO_3-HF; magnification, 100×, reduced 20%.

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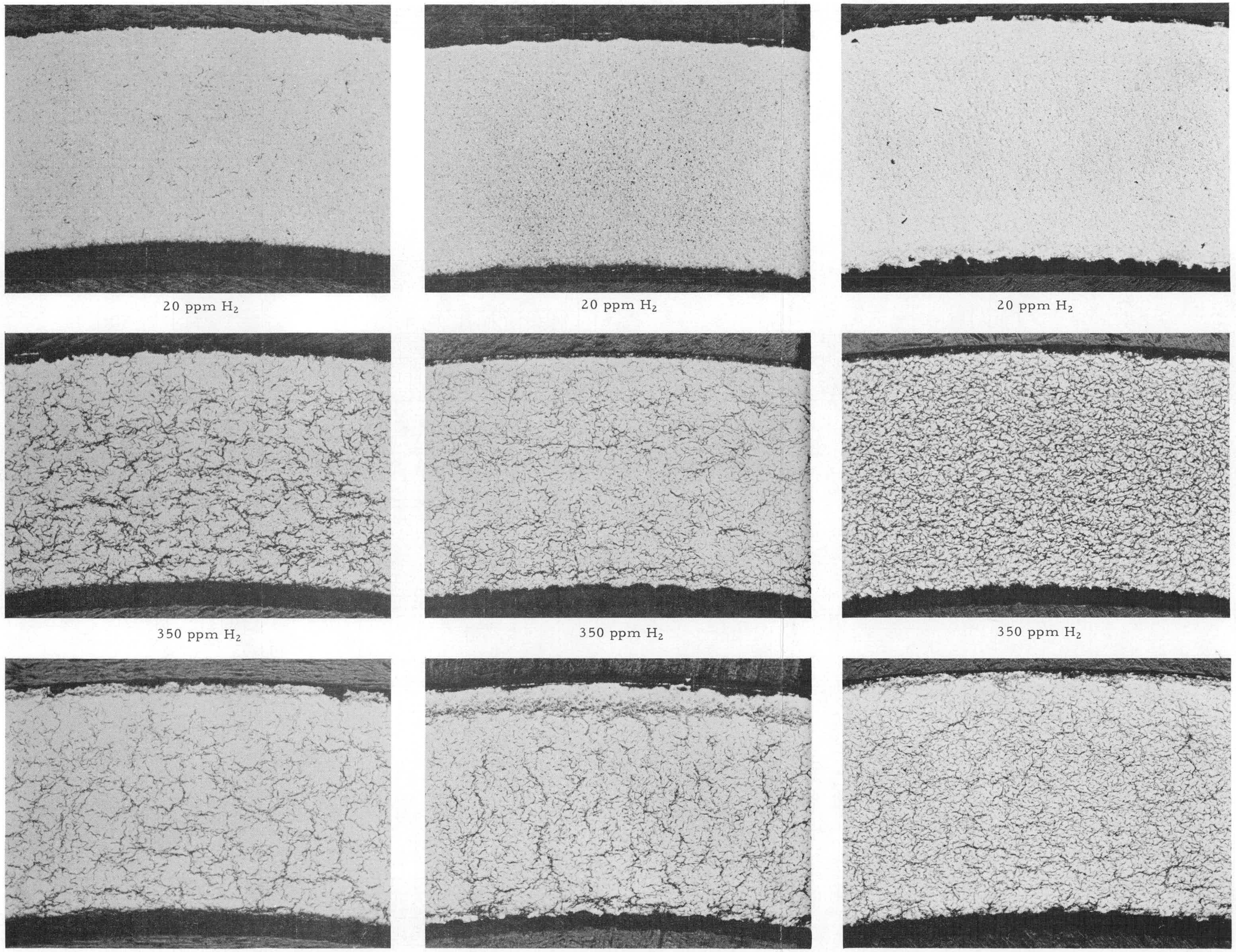
Figure 41. Transverse Sections of Typical Tensile Specimens of Annealed Zircaloy-4 After Test Showing Changes in Hydride Distribution and Orientation



Test Temperature: 70 F

Test Temperature: 650 F

Test Temperature: 800 F

20 ppm H_2

20 ppm H_2

20 ppm H_2

350 ppm H_2

350 ppm H_2

350 ppm H_2

750 ppm H_2

750 ppm H_2

750 ppm H_2

Note: Etch, lactic-HNO_3-HF; magnification, 100×, reduced 25%.

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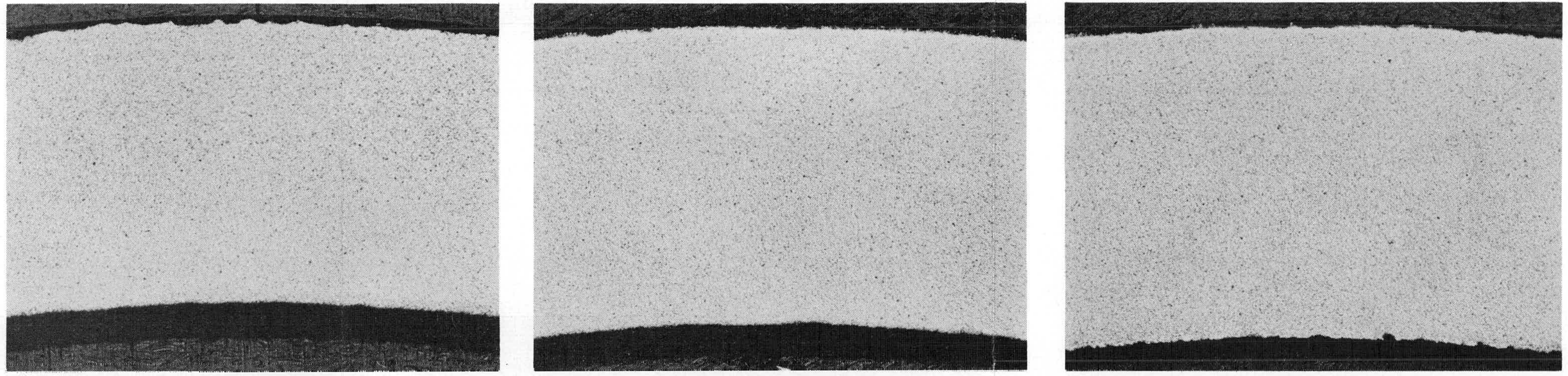
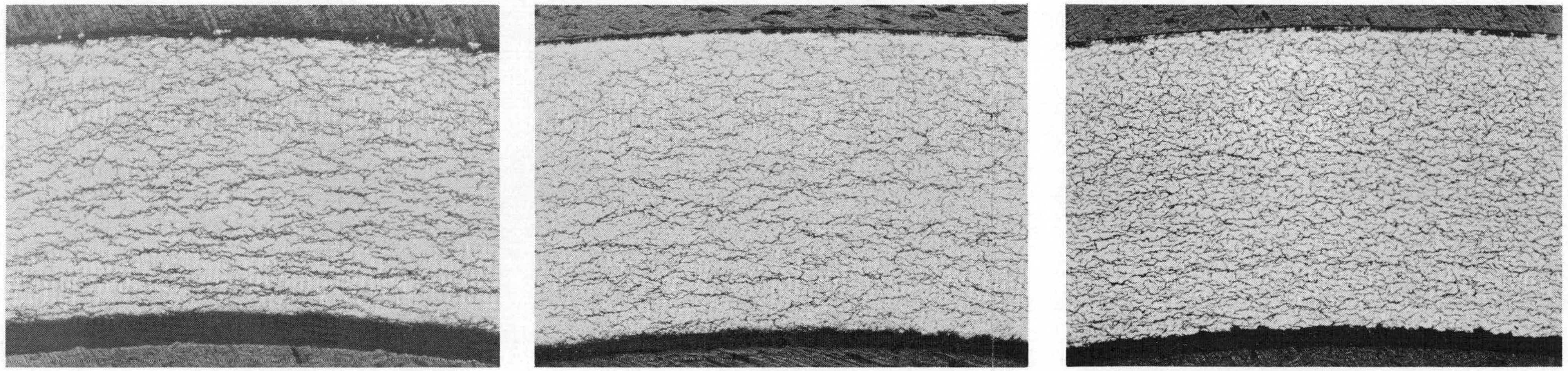
Figure 42. Transverse Sections of Typical Tensile Specimens of Cold-Worked Zircaloy-4 After Testing Showing Changes in Hydride Distribution and Orientation

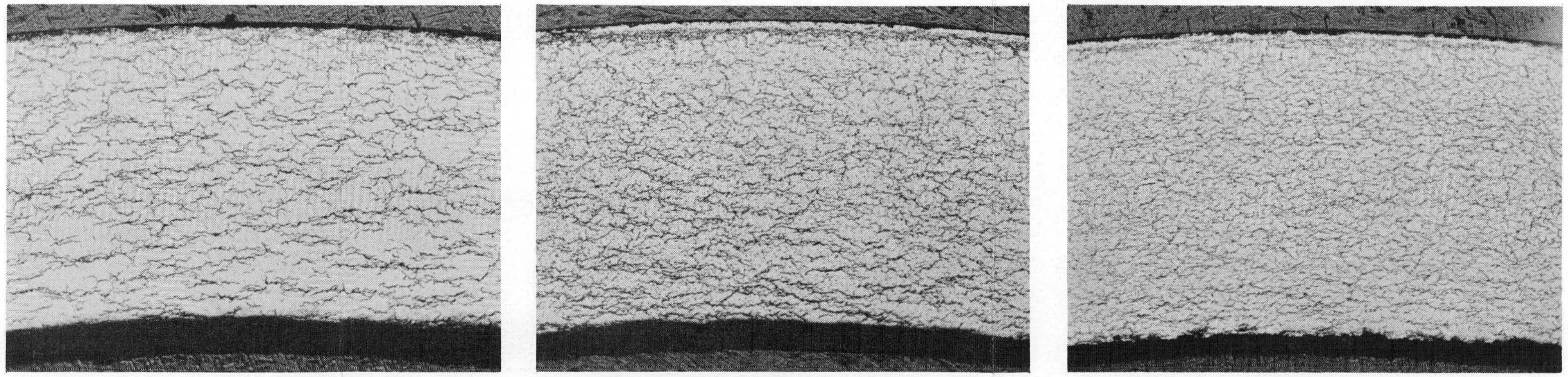
Test Temperature: 70 F | Test Temperature: 650 F | Test Temperature: 800 F



20 ppm H_2 | 20 ppm H_2 | 20 ppm H_2



350 ppm H_2 | 350 ppm H_2 | 350 ppm H_2



750 ppm H_2 | 750 ppm H_2 | 750 ppm H_2

Note: Etch, lactic-HNO_3-HF; magnification, 100×, reduced 25%.

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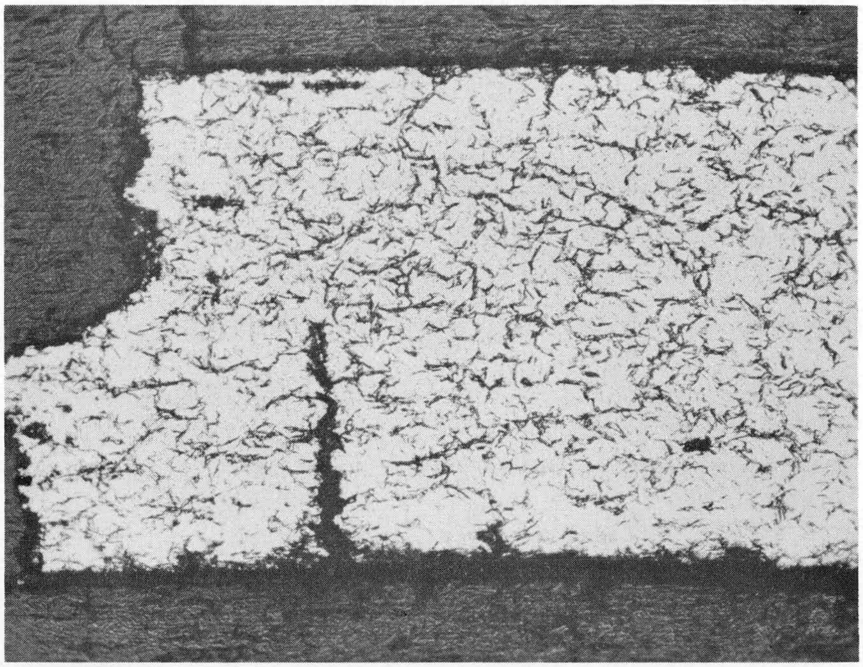
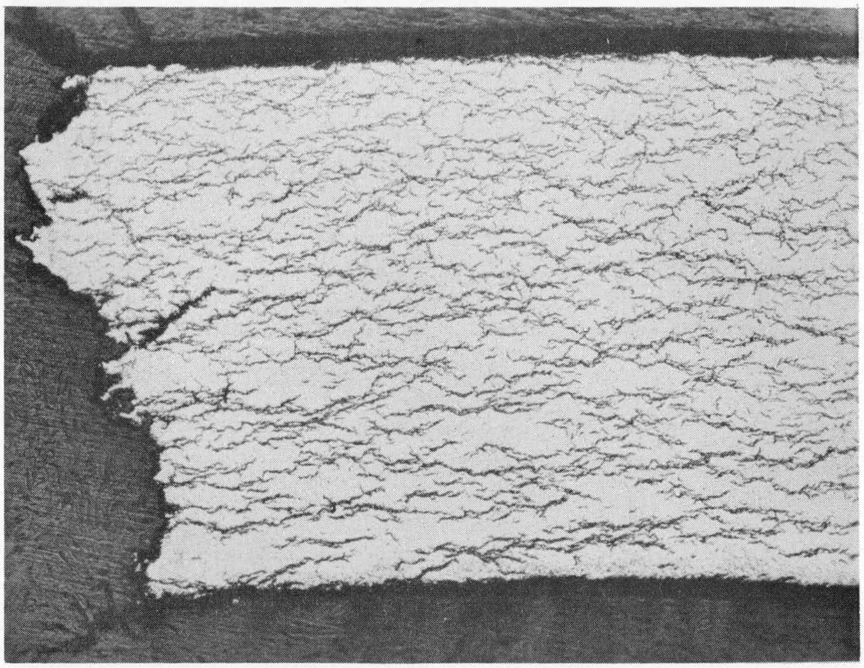
Figure 43. Typical Fractures in Annealed and Cold-Worked Zircaloy-4 Burst-Test Specimens Containing 350 ppm Hydrogen (etch: lactic-HNO_3-HF; magnification: 100×)



Annealed Zircaloy-4



Cold-Worked Zircaloy-4

5. DISCUSSION

The specimens were prepared, and the tests described herein were performed with a minimum of difficulty and without any significantly surprising results. Using full cross-section tubes for tensile testing eliminated possible problems and effects on test results associated with sectioning test strips from the tubes. The hydriding operations proceeded without difficulty, and the desired amounts of hydrogen were introduced uniformly. The time required to reach a stable condition before testing at elevated temperature was not extensive, nor did the high temperatures cause significant hydrogen migration toward the cool grip ends of the tensile specimens.

The tensile-test results illustrate the fact that hydrogen at concentrations below 1000 ppm has little effect on the strength of Zircaloy-4. One interesting observation is that the yield strength of Zircaloy-4 is relatively constant at temperatures between about 550 and 750 F. This is evident particularly with annealed material. The cold-worked material exhibited a relatively sharp decrease in strength at temperatures above 700 F. This deviation may be the result of insufficient stress relief to stabilize the mechanical properties in the temperature range of interest. However, it is more likely that the deviation was caused by the relief of the slight amount of cold-work introduced by cold-straightening the tubing after the 900 F (minimum), 1 hour tempering treatment at the tube mill. The annealed material does not show the same effect because it was annealed in the laboratory without subsequent straightening. In any event, the fact to be recognized is that the strength of cold-worked Zircaloy-4 tubing decreases over the temperature range from 600 to 800 F; the amount of this decrease must be known in order to design the highly rated fuel cladding for pressurized-water reactors.

Burst testing at room temperature did reveal an effect of hydrogen on Zircaloy that was not observed in the tensile-test results: Under the biaxial stress conditions of the burst test, the addition of hydrogen to the material decreased its strength. The decrease was more pronounced in the cold-worked material than in the annealed material, although the effect was observed in each case. The burst strength of the cold-worked material appeared to decrease abruptly with the addition of more than 350 ppm hydrogen, whereas the strength of the annealed material decreased at a fairly uniform rate with increasing hydrogen content.

The anomalous increase in the burst strength of annealed material at the 350 ppm hydrogen level, shown in Figure 37, is undoubtedly the result of cold-working during the test. All three specimens tested at this hydrogen level developed leaks in their end fittings near their maximum pressure capability. Retesting after the leaks were repaired resulted in higher burst pressures. It is postulated that the initial pressurization caused some cold-working, and the resulting strengthening was revealed in the final test to rupture.

An examination of the microstructures of the ruptured specimens provides no rational explanation for the reduced burst strength associated with increases in hydrogen content. It is possible that, under the pneumatically loaded system, the slightest crack in heavily hydrided material will propagate quickly and result in early failure. In contrast, under uniaxial loading in the tensile test, the energy stored in the specimen during the test is not as great as that in the pneumatically loaded burst-test specimen, and therefore there is less tendency to propagate a crack that might start before the ultimate strength of the material is reached. It is also possible that eccentricity in the tube wall allows a slight bending to occur under the biaxial stress conditions of the burst test. The bending strain could exceed the ultimate strength of the material locally, initiating a crack that would propagate rapidly in the hydrogen-embrittled matrix. In any event, the decrease in burst strength at room temperature should be recognized, and precautions should be taken during postoperation fuel handling to prevent bending or shock loading of heavily hydrided fuel cladding.

More work in the area of burst testing is required to evaluate the effects of hydrogen on the elevated-temperature biaxial properties of Zircaloy-4 tubing. The fact that burst strength is reduced by about 25% at room temperature by additions of 1000 ppm hydrogen, while uniaxial tensile strength is relatively unaffected, indicates that elevated-temperature tensile data alone may not provide sufficient insight into the behavior of Zircaloy cladding at reactor operating temperatures for the design of reliable fuel elements.

6. CONCLUSIONS AND RECOMMENDATIONS

The results of the tests described in this report led to the following conclusions:

1. Uniformly distributed hydrogen at concentrations up to 1000 ppm has no significant effect on the longitudinal tensile strength of annealed or cold-worked Zircaloy-4 tubing over the range of temperatures from 70 to 800 F.

2. The total elongation exhibited by annealed and cold-worked Zircaloy-4 tubing is reduced significantly by adding hydrogen to the material. The greatest effect is apparent at room temperature (70 F), where 62% reductions (from 33 to 13%) are noted in annealed material with an increase in the hydrogen concentration from 20 to 1000 ppm. Reductions of 75% (from 16% to 4%) in the elongation of cold-worked material are observed at room temperature. Hydrogen is effective in reducing tensile elongation over the entire temperature range of the tests. However, the extent of the reduction diminishes with increasing temperature, and the net effect is that the tensile elongation of both annealed and cold-worked material containing up to 1000 ppm hydrogen is acceptable (about 10%) in the temperature range of interest.

3. Under the biaxial stress conditions of a pressure burst test at room temperature, hydrogen has a significant degrading effect on the burst strength of both annealed and cold-worked Zircaloy-4. The effect is greatest in cold-worked material, in which burst strength is reduced by about 25% (from 115,000 to 85,000 psi for 0.420-inch-OD by 0.025-inch-wall tubing) with an increase in the hydrogen content from 20 to 1000 ppm. In annealed material the reduction is only 18% (from 88,000 psi to 72,000 psi for 0.420-inch-OD by 0.025-inch-wall tubing).

4. Since the principal stresses in fuel cladding result from external hydraulic pressure and internal pneumatic pressure, further

testing is recommended to establish the effect of hydrogen content on the burst strength of Zircaloy tubing over the entire temperature range of interest for water-reactor fuel cladding.

APPENDIX

Mill Test Reports for Specimen Material

Figure A-1.

ATT: ART LOWE

Calumet & Hecla **WOLVERINE TUBE** DIVISION
9525 BEECH DALY RD., DEARBORN HEIGHTS, MICH. 48125

CHEMICAL AND PHYSICAL REPORT OF MATERIAL SHIPPED

DEARBORN HEIGHTS PLANT

CUSTOMER: BABCOCK AND WILCOX

WOLVERINE ORDER NO. 93591

CUSTOMER ORDER NO.	ITEM	QTY. ORDERED	OD	ID	WALL	LENGTH FEET	LENGTH INCHES	CUSTOMER SPEC. NO.
A-27957-41-1020-20	1	215 PCS	.422	.368		11	11-11/16	

ALLOY ZIRCALOY-4				
SAMPLE INTERVAL				
LOT NO./PIECES	8A24/89			
INGOT & ANNEAL CHARGE	2CH-3984			
INVOICE NUMBER	DH-93591			
CHEMICAL ANALYSIS				
HYDROGEN PPM	11/11			
NITROGEN PPM	44/45			
OXYGEN PPM	1180/1030			
MECHANICAL PROPERTIES & TESTS				
ULTRASONIC TEST (SEE REMARKS)	PASSED			
FLARE TEST TO 15 % of O.D.	PASSED			
FLATTENING TEST TO % of O.D.				
GRAIN SIZE-ASTM NO. TRANS./LONG.				
ROCKWELL SCALE				
HYDROSTATIC TEST 5000 PSI	PASSED			
AIR TEST 100 PSI	PASSED			
CORROSION TEST	MG/DM^2	MG/DM^2	MG/DM^2	MG/DM^2
14 DAY STEAM 1500 PSI 750 °F	23.0/23.8			
DAY WATER PSI °F				
BURST PRESSURE x 10^3 PSI				
BURST YIELD x 10^3 PSI				
CIRCUMFERENTIAL ELONGATION				
ROOM TEMPERATURE				
ELONGATION % in ~~2"~~ 1"	9.0/9.0			
TENSILE STRENGTH x 10^3 PSI	112.0/109.0			
YIELD STRENGTH x 10^3 PSI	85.6/79.8			
HOT TENSILE - TEMPERATURE				
ELONGATION % in 2"				
TENSILE STRENGTH x 10^3 PSI				
YIELD STRENGTH x 10^3 PSI				
HYDRIDE ORIENTATION Fn. NO.				
SURFACE OD/ID RMS	10-15/15-20			

REMARKS ULTRASONIC TESTED LONGITUDINAL & TRANSVERSE OD & ID. ULTRASONIC TEST STANDARD SIZE - .002 DEEP x .250 LONG.

THIS MATERIAL IS HEREBY CERTIFIED IN ACCORDANCE WITH AND CONFORMS TO APPLICABLE REFERENCED SPECIFICATIONS AND ORDERING REQUIREMENTS ASTM B 353-62T COMP/295/0-4/41-0023

ORIGINAL SIGNED BY (METALLURGIST) JOHN W. MERRITT John W. Merritt

SWORN TO BEFORE ME THIS 23rd DAY OF November 19 66 COUNTY OF WAYNE STATE OF MICHIGAN

ORIGINAL SIGNED BY Betty Wilhelm NOTARY PUBLIC MY COMMISSION EXPIRES August 11, 1968

X619 1/66

Figure A-2.

CARBORUNDUM METALS CLIMAX, INC. / P. O. Bo 12 • Akron, New York 14001
Area Code 716 • 542-5454

2CH

WROUGHT PRODUCTS DATA REPORT

USTOMER	Wolverine Tube Division	WEIGHT	1067.0 lbs.
		INGOT NO.	M-952
CUSTOMER ORDER	3937	SIZE	3.915" O.D. x 0.950" I.D. x 10" long
MATERIAL	Zircaloy-4 Grade 34 Zirconium Billets Specifications P & R 222 and 225-M	ITEM	1
		PCS.	40
		CMC ORDER	4746

CHEMICAL COMPOSITION (%)

	Top	2	Middle	34	Bottom
Sn	1.49	1.63	1.46	1.49	1.24
Fe *	0.19	0.24	0.20	0.24	0.21
Cr *	0.10	0.13	0.09	0.10	0.09
Ni					
Sum *	0.29	0.37	0.29	0.34	0.30

IMPURITY ANALYSIS (PPM)

	Top		Middle		Bottom
Al	<20		<20		<20
B	<0.2		<0.2		<0.2
C	96		80		88
Ca	<20		<20		<20
Cd	<0.2		<0.2		<0.2
Cl	<15		<15		<15
Co	<10		<10		<10
Cr					
u	<20		<20		<20
re					
H	8				12
Hf	68		81		87
Mg	<10		<10		<10
Mn	<20		<20		<20
Mo	<20		<20		<20
N	43		36		39
Ni	21		18		14
Na					
O	950	1070	1070	1020	1090
Pb	<20		<20		<20
Si	<30		<30		<30
Sn					
Ti	<20		<20		<20
U	<1				<1
U-235	<.007				<.007
V	<20		<20		<20
W	<50		<50		<50

MECHANICAL PROPERTIES

TENSILE TEST

METHOD ________ TEST TEMP. ________

SPECIMEN ANNEAL TEMP. ________ °F

TIME AT TEMP. ________ MINUTES

SPECIMEN		
LOCATION		
ULTIMATE STRENGTH PSI		
0.2% OFFSET YIELD STR. PSI		
ELONGATION %		
REDUCTION IN AREA %		

HARDNESS

Average Ingot Hardness 160 BHN

I certify that the above analysis is true to the best of my knowledge and belief and the product conforms to the requirements of P & R Specifications 222 and 225-M.

PAGE 1 OF 1

John H Schmid DATE MAY 18 1966

CM 140 4-66

REFERENCES

[1] Lyman, L. R., Metallurgical Examination of PWR Core 1 Blanket Fuel Rods at End of Third Seed Life, Westinghouse Atomic Power Division, WAPD-TM-433, August 1964.

[2] Anderson, R. H., Jr., Harbinson, E. N., and Lowe, A. L., Jr., The Effect of Hydrogen on the Mechanical Properties of Zircaloy-4, The Babcock & Wilcox Company, BAW-277, Lynchburg, Virginia, June 1965.

[3] Winton, J., A Method for Gas Hydriding Zirconium Alloys at 400 C, United Kingdom Atomic Energy Authority, Reactor Materials Laboratory, 1966 (TRG Report 1255).

[4] Mishima, V., *et al.*, "An Experimental Study on the Mechanical Strength of Fuel Cladding Tubes Under Loss-of-Coolant Accident Condition in Water-Cooled Reactors," 1964 Geneva Conference Paper P/438 (1964).

[5] Burton, H. H., Hydrogen Effects on Zircaloy-2 Tensile Properties, HW-61077, July 10, 1959.

[6] Mudge, W. L., Jr., "Effect of Hydrogen on the Embrittlement of Zirconium and Zirconium-Tin Alloys," *Zirconium and Zirconium Alloys*, ASM Symposium, 146 (1953).

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