



# Fracture strength of hydride precipitates in Zr–2.5Nb alloys

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## Abstract

The hydride precipitate fracture strength as a function of precipitate size and temperature (23–250°C) in smooth tensile specimens of Zr–2.5Nb pressure tube material (nominal hydrogen content 100 ppm by weight) was studied using the acoustic emission technique. At room temperature, this strength is sensitive to hydride length when the average hydride length is short, and is insensitive to the hydride length when the average hydride length is longer than 25 μm. The hydride fracture strength decreases slightly with temperature, but a more rapid decrease in the yield strength offsets this decrease, resulting in a brittle-to-ductile transition at 120°C to 140°C in smooth tensile tests. The presence of hydrides causes a decrease in the ultimate tensile strength of the material at low temperatures, and has no effect at high temperatures for these smooth tensile specimens. Crown copyright © 1999 Published by Elsevier Science B.V. All rights reserved.

## 1. Introduction

The potential fracture of hydride precipitates in zirconium alloys has been a concern for the material's application in the nuclear industry. When the bulk hydrogen isotope concentration exceeds a certain level that allows the formation of hydride precipitates, these alloys are susceptible to a crack initiation and propagation process called delayed hydride cracking (DHC) [1]. In the current DHC initiation models [2,3], one of the key parameters is the fracture strength of hydrides, denoted by  $\sigma_f^h$ . For example, the theoretical value for the ultimate threshold stress intensity factor for DHC initiation at a sharp crack tip,  $K_{IH}$ , is given by

$$(K_{IH})^2 = \frac{E^2 \varepsilon_{\perp} \tau}{8\pi(1 - \nu^2)^2 \left( \frac{1}{1 - 2\nu} - \sigma_f^h / \sigma_y \right)}, \quad (1)$$

where  $E$  is Young's modulus,  $\nu$  is Poisson's ratio,  $\sigma_y$  is the yield strength of the matrix material,  $\varepsilon_{\perp}$  is the stress free strain of the hydride precipitate in the plate normal direction, and  $\tau$  is the hydride precipitate's thickness.

The critical hydride length for DHC initiation at a notch or crack tip,  $L_C$ , is determined by

$$L_C = \frac{\alpha E \varepsilon_{\perp} \tau}{(1 - \nu^2) \left[ \sigma_{yy}^{\max} - \sigma_f^h \right]}, \quad (2)$$

where  $\alpha$  is a proportionality factor and  $\sigma_{yy}^{\max}$  is the maximum tensile stress normal to the cracking plane acting on the hydrides at the notch or crack tip.

Unfortunately, there are very little data in the literature that directly give either the tensile or the fracture strength of zirconium hydride. This is partially due to the difficulty of preparing suitable solid zirconium hydride specimens. The early work of Barraclough and Beevers [4], based on uniaxial compression tests on ZrH<sub>1.66</sub> bulk specimens shows that  $\sigma_f^h$  may be in the range of 100–200 MPa in the temperature range between 22°C and 453°C. A few years ago, Puls et al. [5] conducted a series of confined and unconfined compression tests at temperatures between 50°C and 400°C for solid zirconium hydride specimens of macroscopic size having stoichiometric compositions ranging from ZrH<sub>1.2</sub> to ZrH<sub>1.9</sub>. They found that for most of the specimens, the yield strength of these solid hydride specimens ranged from about 600 MPa at 50°C to about 250 MPa at 400°C. At room temperature, yield strength values in the range from 730 to 1000 MPa were obtained. In a number of unconfined room temperature compression tests, fracture of the hydride samples

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occurred at approximately 750 MPa. However, these types of tests cannot be used to give reliable results of the fracture strength of a hydride platelet confined in a zirconium matrix. Choubey and Puls [6] used acoustic emission to detect the onset of cracking in long hydride platelets in tensile specimens of Zr–2.5Nb pressure tube material, over a range of temperatures. These acoustic emission tests were an extension of earlier room temperature tests [7,8]. The results, when combined with estimates of the compressive transformation stress inside the hydride obtained from elastic–plastic finite element calculations [9], suggest that a lower-bound value for the fracture strength of a hydride platelet ranges from 600 to 520 MPa between ambient and 100°C, respectively.

In this report, the experimental method of Choubey and Puls [6] is used to study the dependence of  $\sigma_f^h$  on the size of hydride platelets and on the temperature.

## 2. Experimental procedure

Cold-worked Zr–2.5Nb pressure tube material was flattened and machined into smooth tensile specimens with the tensile axis in the tangential direction of the pressure tube from which the material was taken. To minimize the influence of curvature on the specimens, the thickness of the gauge region was not reduced but the width was reduced until the cross-section area was the same as that used by Choubey and Puls [6]. The material contains about 2.4–2.8 wt% Nb, 900–1300 wt ppm O and less than 10 wt ppm H.

The test specimens were hydrogenated at 400°C by a gaseous method to increase the nominal hydrogen concentration to 100 wt ppm (about 0.9 at%), followed by homogenizing at 400°C for 10 days. To produce radial–tangential (relative to the pressure tube) hydrides with different average lengths, hydrides were reoriented by tensile stress under different cooling rates by varying the time (0.07–24 h) to decrease the temperature from 360°C to 50°C. In Choubey and Puls' hydride reorientation method, the applied stress during cooling was always kept at 50 MPa below the yield strength of the material at any given temperature. One of their specimens failed by hydride cracking during a long cooling period, which indicates that the stress level at low temperatures might have been higher than the hydride fracture strength ( $\sigma_f^h$ ). For the purpose of reorienting hydrides without cracking them before the acoustic emission tensile tests, the following tensile stress formula was used during the re-orientation procedure:

$$\sigma \text{ (MPa)} = 594 - 0.5848 \times T \text{ (}^\circ\text{C)}. \quad (3)$$

This formula gives tensile stress levels about 160 MPa below yield at 50°C, 60 MPa below yield at 300°C, and 40 MPa below yield at 360°C, respectively.

The specimens were tested in tension at a constant engineering strain rate of approximately  $4 \times 10^{-4} \text{ s}^{-1}$ . The experimental details of the acoustic emission (AE) are described elsewhere [6]. Two AE sensors are attached at the pin-hole locations to detect the AE signals from the gauge region. Usually, each pin-hole region will generate spurious AE signals during the test. In principle, most of these spurious signals can be eliminated by examining the coincidence of arrival of the pulses at the two AE sensors. Coincident signals represent a real 'event'. However in practice, since the spurious signals from the two pin-hole regions can occur quite often, occasionally, two spurious signals from each pin-hole region, or reflections and recombinations of these signals, may occur at the same time, so that the computer considers it to be a 'true' signal from the gauge region. To determine the true onset of the hydride cracking events in the gauge region, we use the procedure of Choubey and Puls [6]. This procedure assumes that the true hydride cracking initiation point is signaled on the cumulative AE events versus time plots by the starting point of a rapid and continuous increase in the AE event rate relative to the more intermittent rate obtained during the earlier stage; see Fig. 1, for example. The tensile stress level at the initiation point of hydride cracking is denoted as the global hydride fracture strength,  $\sigma_f$ .

Generally, one would expect that the fracture strength of hydrides ( $\sigma_f^h$ ) is not equal to  $\sigma_f$ . The stress,  $\sigma_f^h$ , is defined as the stress *acting locally on the hydride* to cause its fracture, while  $\sigma_f$  is the stress *acting globally on the tensile specimen* at which hydrides start to fracture. Two factors can cause these two stresses to be different. First, if the zirconium hydride has different elastic properties than the zirconium matrix, the values of  $\sigma_f$

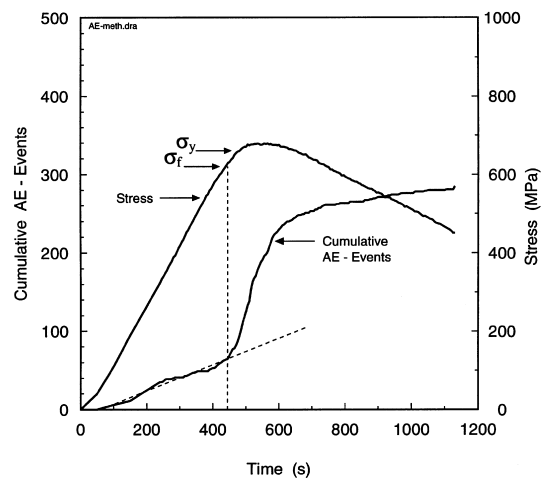


Fig. 1. The method of determining the onset of hydride cracking [6].

Table 1  
Measured hydride platelet dimensions in specimens with a nominal hydrogen concentration of 100 wt ppm (~0.9 at%)<sup>a</sup>

Cooling time (h)	$L_{ave}$ ( $\mu\text{m}$ )	Standard deviation in $L_{ave}$ ( $\mu\text{m}$ )	$L_{max}$ ( $\mu\text{m}$ )	Maximum hydride thickness <sup>b</sup> ( $\mu\text{m}$ )	Ratio of thickness to length <sup>c</sup>
0.07	4.7	2.0	10	1.3	0.13
2.5	23.3	15.6	70	3.5	0.05
6.0	53.9	35.7	170	4.0	0.024
8.0	43.9	25.3	140	5.0	0.036
12.0	84.5	54.0	230	5.0	0.022
24.0	62.1	46.7	210	9.0	0.043

<sup>a</sup> The length of the platelet measured is that in the pressure tube's axial direction, which is the longest of the two platelet directions.

<sup>b</sup> Due to the etching technique, the uncertainty in the measurements of hydride thickness is high as compared to the measurements in hydride length.

<sup>c</sup> The ratio is calculated using maximum thickness and maximum length ( $L_{max}$ ). However, the thickest hydride may not have the longest length.

and  $\sigma_f^b$  can be different because of a misfit stress induced on the hydride by the applied stress which will alter the net stress acting on it [8]. However, limited experimental evidence indicates that the hydride elastic properties are close to those of the zirconium matrix. Second, the volume expansion during hydride formation initially introduces a compressive stress inside the hydride. This compressive stress would serve to oppose the globally applied tensile stress needed to bring the stress acting on the hydride to the fracture strength. As will be seen in this experiment, this compressive stress is likely negligible when hydrides are reoriented under tensile load and grow to more than 25  $\mu\text{m}$  in length.

After the tensile tests were completed, the lengths of hydride platelets in the pressure tube's axial direction were measured. (Note that the hydride's length in the axial direction is greater than its length in the pressure tube's radial direction.) The average and maximum hydride lengths, and the maximum hydride thickness were obtained (see Table 1).

### 3. Results and discussion

#### 3.1. Results at room temperature

The tensile stress at the initiation of hydride cracking at room temperature is plotted against the maximum hydride length,  $L_{max}$ , (Fig. 2) and the average hydride length,  $L_{ave}$ , (Fig. 3). Also shown in Figs. 2 and 3 are the values of the yield strength ( $\sigma_y = 760 \pm 15$  MPa, at 0.2% offset) and the stress levels at the first AE event for as-received Zr-2.5Nb materials. The data are listed in Table 2.

It can be seen that the tensile stress for hydride cracking ( $\sigma_f$ ) is sensitive to the hydride size when  $L_{max} < 70$   $\mu\text{m}$ , or when  $L_{ave} < 25$   $\mu\text{m}$ . A least square fit to the experimental data in this range gives

$$\sigma_f \text{ (MPa)} = 767.47 - 1.567 \times L_{max} \text{ (}\mu\text{m)},$$

$$(L_{max} < 70 \mu\text{m}) R^2 = 0.98, \quad (4)$$

or

$$\sigma_f \text{ (MPa)} = 770.9 - 4.85 \times L_{ave} \text{ (}\mu\text{m)},$$

$$(L_{ave} < 25 \mu\text{m}) R^2 = 0.99, \quad (5)$$

where  $R$  is the correlation factor. When the average hydride length increases from about 25  $\mu\text{m}$  to about 85  $\mu\text{m}$ , the hydride fracture stress fluctuates at roughly the same level. This is evidence that the fracture strength is insensitive to the size of the hydrides above about 25  $\mu\text{m}$ , i.e.,

$$\sigma_f \text{ (MPa)} = 644.4 \pm 45, \quad (L_{ave} > 25 \mu\text{m}). \quad (6)$$

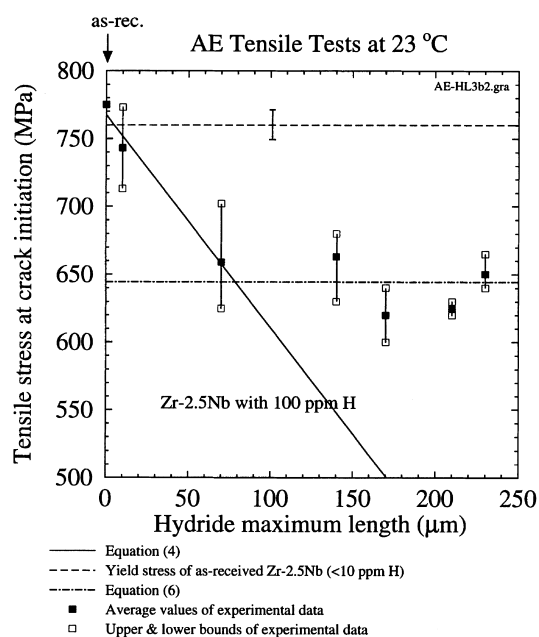


Fig. 2. The fracture strength of hydrides as a function of maximum hydride length.

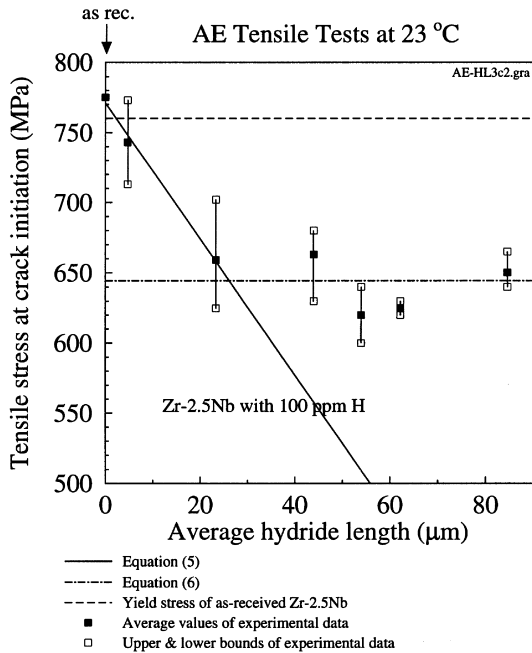


Fig. 3. The fracture strength of hydrides as a function of average hydride length.

The insensitivity of  $\sigma_f$  to hydride length when  $L_{ave} > 25 \mu\text{m}$  implies that the stress contribution from the hydride formation process (volume expansion resulting in compression) is smaller than the experimental uncertainty and, therefore, can be ignored for long hydrides. The reason for this insensitivity to the hydride length for  $L_{ave} > 25 \mu\text{m}$  may be partly due to the fact that the hydride aspect ratio (thickness to length ratio) drops at this length by about an order of magnitude and then remains essentially constant with increase in the hydride length (Table 1). Numerical analysis has shown [6] that for a hydride aspect ratio of 0.04–0.02, the minimum normal stress in the hydride ranges from about  $-350$  to  $-175$  MPa. The actual compressive stress in the hydrides that fracture at  $\sigma_f$  is likely lower

than this considering that  $\sigma_f$  is the tensile stress at the onset of hydride fracture which is expected to always start at the weakest hydrides having dimensions that would have lower local residual compressive stresses than the values calculated for the hydrides with average dimensions. On the other hand, for hydrides with aspect ratio greater than 0.1, the internal compressive stress inside the hydride would be so high that  $\sigma_f > \sigma_y$  in which case the plastic deformation in the matrix during testing would be necessary to induce a tensile stress inside the hydride high enough to overcome the initial compressive stress and fracture the hydride. However, at higher temperatures, as  $\sigma_y$  decreases with temperature, the high plastic deformation, generated locally in the region where the specimen ultimately fractures, may not be able to induce sufficient tensile stress inside the hydride to fracture it before the hydride is able to 'flow' with the matrix and reorient itself such that the longer platelet length is in the tensile stress direction (see [6]). After flow re-orientation into this direction, at a certain plastic strain, no further re-orientation of the hydride is possible and the hydride will eventually fracture in the through-thickness direction as the plastic strain in the matrix increases.

These results are consistent with early observations [7,8] that a higher stress level is needed to crack small hydrides, and essentially no plastic strain is needed to fracture large hydrides at room temperature. Experimental scatter of the data may be due to variations in the internal residual stress, hydride aspect ratio and the uncertainties in the determination of the time for the start of AE events that are due to hydride cracking.

The ultimate tensile strength ( $\sigma_u$ ) has also been measured and is plotted against the average hydride length in Fig. 4. All hydrided specimens broke at the maximum load at room temperature, while the as-received Zr–2.5Nb material with less than 10 wt ppm of hydrogen did not fail at its ultimate tensile strength. A linear fit to the data yields

$$\sigma_u \text{ (MPa)} = 792.4 - 1.442 \times L_{ave} \text{ (}\mu\text{m)}, \quad R^2 = 0.74. \quad (7)$$

Table 2  
 $\sigma_f$  and  $\sigma_u$  measurements at room temperature for smooth tensile specimens

Cooling time (h)	$\sigma_f$			$\sigma_u$		
	Lower bound	Average (MPa)	Upper bound	Lower bound	Average (MPa)	Upper bound
As-received <sup>a</sup>	—	—	—	788	810	832
0.07	713	743	773	766	774	782
2.5	625	659	702	759	767	780
6.0	600	620	640	624	674	728
8.0	630	663	680	740	748	757
12.0	640	650	665	687	704	736
24.0	620	625	530	672	677	682

<sup>a</sup>The as-received material has a hydrogen concentration less than 10 wt ppm.

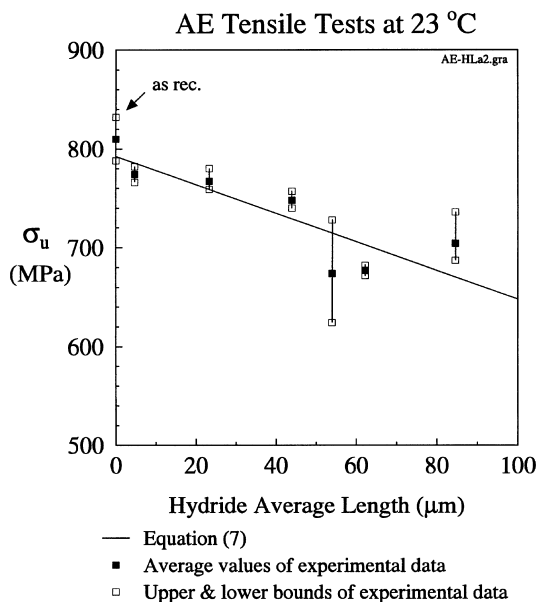


Fig. 4. The ultimate tensile strength of hydrided Zr-2.5Nb as a function of average hydride length.

### 3.2. Results at elevated temperatures

The fracture strength of hydrides was measured in the temperature range from room temperature to 250°C. The cooling time during the hydride reorientation for specimens in this set of measurements was fixed to 12 h. Results are summarized in Table 3. Like the results of Choubey and Puls [6] and the original findings of Evans and Parry [10] for Zircaloy-2, a brittle-to-ductile transition was observed at the temperature range from 120°C to 140°C. Below the transition temperature, specimens failed by brittle hydride fracture at the maximum load. Some hydrided specimens failed before reaching 0.2% yield. At 125°C, the hydrided specimen did not fail at  $\sigma_u$ , indicating a transition from brittle to

ductile behavior. Above the transition temperature, there is no indication of hydride fracture even well after yielding of the bulk material. Fig. 5 shows the measured fracture strength of hydrides, along with the measured yield strength (at 0.2% offset) of the material in the transverse direction. A linear fit gives

$$\sigma_f \text{ (MPa)} = 650.84 - 0.09096 \times T \text{ (}^\circ\text{C)},$$

$$R^2 = 0.77, \quad (8)$$

and

$$\sigma_y \text{ (MPa)} = 782.69 - 1.0254 \times T \text{ (}^\circ\text{C)},$$

$$R^2 = 0.97. \quad (9)$$

The cross-over point of these two lines (the brittle-to-ductile transition point) is at about 140°C, which is a

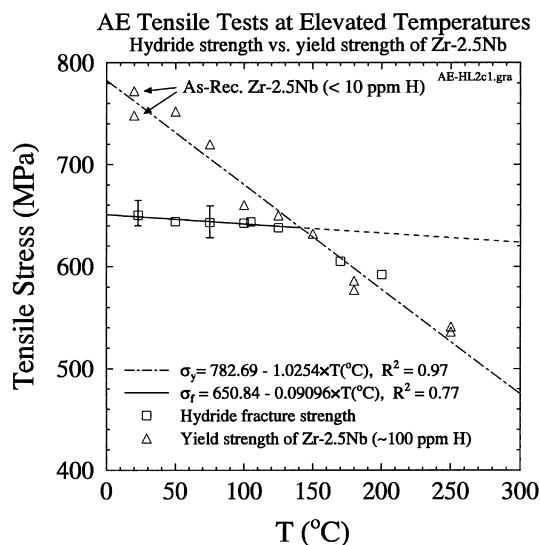


Fig. 5. The fracture strength of hydrides and the yield strength of Zr-2.5Nb as a function of temperature.

Table 3  
 $\sigma_f$  and  $\sigma_u$  at elevated temperatures for smooth tensile specimens

T (°C)	Type of specimens	$\sigma_f$ (MPa)	$\sigma_y$ (0.2%) (MPa)	$\sigma_u$ (MPa)	Break at $\sigma_u$
23	As-received	—	772	797	No
23	As-received	—	748	772	No
23	Hydrided	650	Failed before 0.2% yield	704	Yes
50	Hydrided	644	752	752	Yes
75	Hydrided	643	720	725	Yes
100	Hydrided	643	660	663	Yes
105	Hydrided	644	Failed before 0.2% yield	664	Yes
125	Hydrided	638	650	654	No
150	Hydrided	—	632	635	No
180	Hydrided	—	577	581	No
180	Hydrided	—	586	589	No
250	As-received	—	536	568	No
250	Hydrided	—	541	546	No

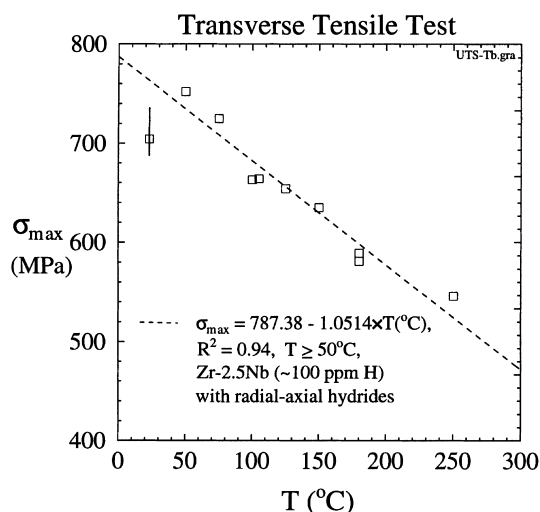


Fig. 6. The ultimate tensile strength of hydrided Zr-2.5Nb as a function of temperature.

good indication that the measured fracture strength of hydrides is in the right range (otherwise, if the fracture strength of the hydrides were much lower, then the cross-over point would shift to much higher temperatures). It is evident the reason for no hydride cracking at higher temperatures is that the material yields at a lower stress level than the hydride fracture strength (i.e.,  $\sigma_y < \sigma_f$ ) and the induced hydride misfit strain resulting from the matrix plastic strain is not able to raise the internal hydride stress above the hydride's fracture strength prior to it being reoriented by flow. To measure the fracture strength of hydrides at higher temperature, the yield strength of the material has to be increased (the yield strength of fully irradiated materials is much higher than unirradiated materials), or stress concentrators such as notched specimen are required to raise the stress level above the yield strength at the notch-tip hydrides.

Fig. 6 shows the  $\sigma_u$  of hydrided specimens (each containing a similar hydride size distribution) as a function of temperature. An increase of  $\sigma_u$  at about 50°C from room temperature is observed. Compared to as-received material,  $\sigma_u$  decreases significantly at room temperature and less significantly at high temperatures (see Table 3). A least square fit to the  $\sigma_u$  data of hydrided material at temperatures higher than 50°C results in

$$\sigma_u \text{ (MPa)} = 787.38 - 1.0514 \times T \text{ (}^\circ\text{C)},$$

$$R^2 = 0.94. \quad (10)$$

#### 4. Conclusions

1. The applied tensile stress to fracture hydrides at room temperature is a function of hydride length when the

average hydride length is less than 25  $\mu\text{m}$ , and is insensitive to the hydride length when the average hydride length is longer than 25  $\mu\text{m}$ .

2. The hydride fracture strength decreases slightly with temperature between room temperature and 125°C. However, a much faster decrease in the yield strength of the zirconium alloy results in a brittle-to-ductile transition at 120°C to 140°C in smooth tensile specimens.
3. The presence of hydrides causes a decrease of  $\sigma_u$  at low temperatures and has a small effect on  $\sigma_u$  at high temperatures for smooth tensile specimens.
4. In order to measure the fracture strength of hydrides at higher temperatures (>125°C), irradiated materials or specimens with stress concentrators (such as notches and cracks) need to be used for testing. However, in the latter case, the present method would not work too well, since it relies on reliably locating the time (stress) at the start of the increase in cumulative acoustic emission counts due to hydride cracking. To be meaningful and sufficiently sensitive, this method requires that a large number of hydrides under the same global stress state be available for potential fracture.

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