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HYDROGEN EMBRITTLEMENT TESTING OF A ZIRCONIUM BASED ALLOY

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Hydrides, Hydrogen, Mechanical Testing, Ductile-Brittle Testing

Abstract

Nuclear fuel rods in power reactors are typically clad with zirconium based alloys. These materials undergo corrosion and consequent hydriding during reactor operation. . Due to limited storage space in the utilities' spent fuel pool for used and discharged fuel, many of the utilities are implementing dry cask storage. There is a concern that the relatively high temperature drying process for dry storage coupled with the nascent hydrides and internal gas pressures, may promote radial hydride reorientation that is favorably oriented to promote clad cracking clad breach during storage, transport and handling. This presentation will describe a method for hydrogen charging zirconium alloy tubes with gaseous hydrogen, internally pressurizing the tubes and developing a susceptible microstructure, and conducting mechanical property tests. This research shows that stress, hydrogen level, and testing method influence the ductile to brittle transition temperature.

Introduction

Based on the desirable combination of neutronics, mechanical and physical characteristics zirconium based alloys are used almost exclusively as clad for commercial nuclear fuels. During operation the clad is exposed to reactor coolant and has a resultant oxidation/corrosion rate. The clad oxidation results in hydrogen generation and about 20 % (or less) of the hydrogen is absorbed into the clad This absorbed hydrogen precipitates typically as circumferentially oriented hydrides due to the thermal gradient across the clad wall and the alloy microstructure. During drying for storage at temperatures limited to 400°C, the increased temperature causes hydrogen over approximately 200 wppm, the solubility limit of H at 400°C to go into solution. As the clad cools the H reprecipitates as hydrides. The hydride morphology and location of the new hydrides are strongly influenced by the hoop stress, existing hydride morphology, grain morphology, crystallographic texture, clad wall temperature differential cooling rate, and alloy chemistry. Hydrides precipitating in a radial orientation can adversely affect the ductility. Hydrogen and hydrides can act to challenge the handling of the fuel, post-discharge. A challenge to handling is the effect of hydrides on the ductile to brittle transition temperature (DBTT). For fuel handling and transport, it is important to know if the clad is above or below the DBTT. The DBTT is alloy, microstructure, hydrogen level, stress/strain state, and irradiation damage dependent, along with some sensitivity to strain rate. Current data generation suggests that the DBTT for irradiated cladding is in the range of 100° to 300°C.

During reactor operation there is a hoop stress present in the clad but the temperature gradient is also significant and relatively little radial hydride orientation is observed in operating or discharged fuel. During the long term storage drying process the temperature gradient in the clad is relative low and it is postulated that some radial reorientation may occur. The degree of radial hydriding is dependent on many factors including hydrogen content, temperature and hoop stress. These variables are interest since the radial hydride morphology is well known to be significant to lower the DBTT as evaluated in RCT [1]. Less known is the effect of loading mode. For example, the question is "what is the effect on DBTT from a bending load vs a crush load is unanswered. The objective of this paper is to provide insights to that question by describing a vacuum charging method to obtain hydrogen contents that are consistent with low to high burn up fuel, an aging or radial hydride growth treatment, and chemical and ring compression mechanical properties.

Experimental

Stress relief annealed (SRA) ZIRLO™, an alloy developed by Westinghouse, was used for this study. The nominal composition of ZIRLO is 1% Sn, 1% Nb, 0.1% Fe, and 0.1-0.14% O. The clad was 9.5 mm OD and 8.5 mm ID (0.375 inch OD and 0.330 inch ID). Samples from 0.76 to 38 cm in length were charged depending on the sample disposition.

High purity hydrogen and high purity argon, 99.95% purity, were used to charge and "age" the ZIRLO tubes.

Samples of the desired length were cut from the production tubes using a tubing cutter. The area designated for hydrogen charging was lightly abraded on OD surface using 600 grit silicon carbide paper; the samples were mounted in a simple handheld drill and rotated while the paper was held firmly against the surface. The samples were then wiped with absolute (200 proof) alcohol on a KimWipe until no observable residue was removed. It took between two and three wipes to achieve this level of cleanliness. The cleaned samples were placed in a stainless steel based tube furnace and evacuated within 20 minutes, consistent with a process developed for Zirloy-4 [1]. The samples were evacuated for a minimum of 12 hours prior to the introduction of hydrogen.

A rate of rise (ROR) test was conducted on the system with an allowable pressure increase of 0.05 mTorr in ten (10) minutes, which translates into a leak rate of $4x10^{-8}$ cc He/s. It was determined that rates higher than this resulted in poor absorption of hydrogen; if the system did not pass the ROR it was repeated after additional evacuation, if it still did not pass, the entire manifold, see Figure 1, was heated to about 120°C and the furnace was heated to 450°C for at least 16 hours. After the ROR, the system was evacuated for ten minutes, which decreased the pressure to nominally the same pressure as that noted prior to the ROR. The sample valve (V_S) was closed and the balance of the manifold was purged with hydrogen (V_{H2}) and evacuated three times (V_{vac}). The calibrated volume was then charged to the required pressure to achieve nominally 800 wppm H in the ZIRLO tubing samples. The appropriate valve alignment was determined for either small (V_{Vs}) or larger calibrated volumes (V_{Vs} and V_{Vl}) and the system was evacuated to remove the unneeded hydrogen. The vacuum and hydrogen source valves were closed and the sample valve was opened. The furnace tube was heated to 400°C at a rate of 10°C/min, held for 30 minutes, and then cooled at a rate of 5C/min to 100°C and allowed to convectively cool to RT. The temperature and pressure were monitored and digitally recorded. The system was evacuated after reaching room temperature and the samples were removed.

Swagelok® fittings, 3/8" stainless steel, were attached to the ends of the tubes, one end was capped and the other was attached to fittings with an analog and digital pressure gauge and a ball valve. The sample was then pressurized with 50 to 2000 psi argon and bubble leak tested. If the sample passed leak testing, the sample was purged three times with argon at the desired "aging" temperature. After the third purge, the sample was loaded with the required pressure to achieve the desired stress for the radial hydride growth treatment (RHGT); higher pressures than indicated by Boyles' law were needed since the entire system volume was not heated. The sample was inserted into the furnace and the furnace was heated to 400°C at a rate of 10°C/min, held for one hour, and cooled at a rate of 5°C/hr to 200°C; Figure 2 shows the sample configuration for RHGT). During this 40 hour cooling period, the temperature data were digitally recorded and the pressure data were manually recorded. The pressure was released from the sample after it had reached room temperature. This method of inducing the stress for radial hydride growth causes a decreasing pressure, and consequently hoop stress, with exposure.

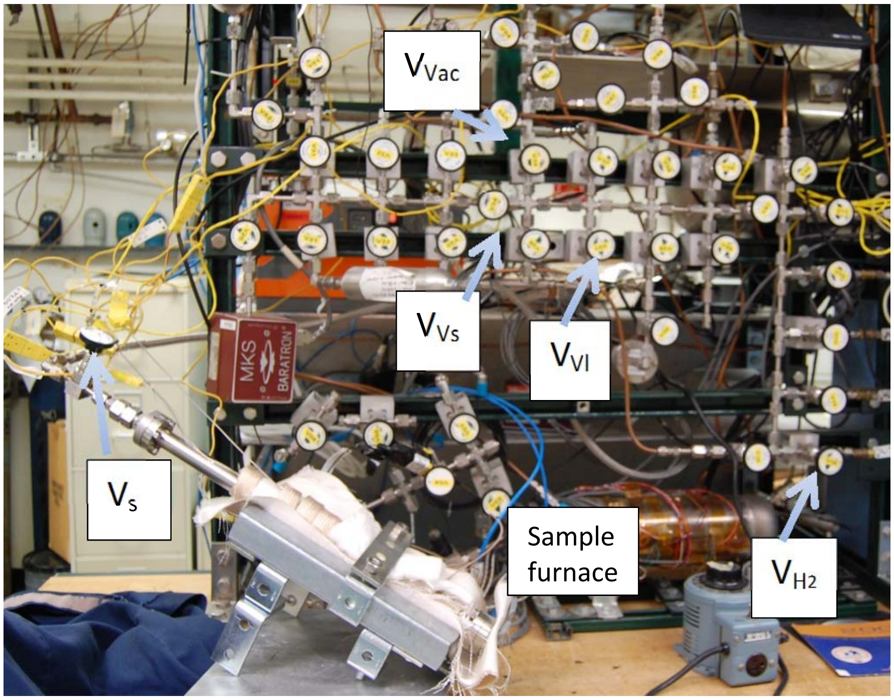


Figure 1. Sample charging station used for these experiments. V_s = Sample valve V_{Vs} = Small calibrated volume valve V_{Vl} = Large calibrated volume valve V_{Vac} = Vacuum valve V_{H2} = Hydrogen source valve

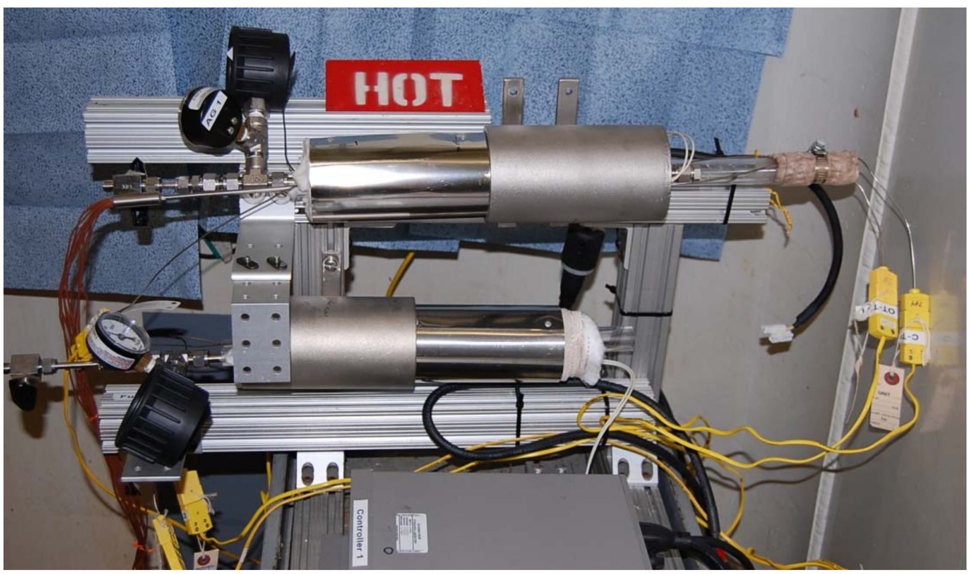


Figure 2. Radial hydride growth treatment system. (a) shows the tubing and gauges (b) shows the aging furnaces with tubing systems being charged.

Hydrogen content was determined using inert gas fusion. Samples that had been charged with target contents of 200, 400, and 800 wppm and one 800 wppm sample that had been charged and aged were wire electrical discharge machined (EDM) into 8 mm long segments. The segments were cut in half axially prior to analysis.

Mechanical properties were determined using three point bend (TPB) and ring compression testing (RCT). Neither of these tests conforms to ASTM standards but each is developmental, and the RCT was conducted in a manner consistent with other researchers [1]. TPB and RCT were conducted at constant crosshead speeds of 5 mm/s. For the RCT this translates into a nominal initial strain rate of 0.525 mm/mm/s and 0.0056 mm/mm/s for the TPB. The crosshead speed (5 mm/s) was close to the maximum that the load frame was capable of achieving. The three point bend tests used a span of 92 mm. The stationary supports were 3 mm diameter and the upper roller was 32 mm. Preliminary efforts revealed that the tube had to be filled to avoid buckling. Quarts rods 8 mm in diameter were cut to 12 mm lengths and loaded into the tube. The ends were unconstrained and there was some gap between the ID of the tube and the OD of the pellets. Data were captured at a rate of 500 Hz for both test types.

Results

Hydrogen charging manifold used for these experiments is shown in Fig. 1. The charging volume is determined by the valve alignment. The pressure and temperature profiles for three samples charged to 800 wppm are shown in Figure 3. Note that the pressure increases with temperature until the furnace reaches approximately 320°C then there is a fairly rapid decrease in pressure as the hydrogen is absorbed by the samples. Virtually all the samples exhibited this absorption behavior with hydrogen absorption becoming obvious around 300°C. Figure 4 shows the pressure temperature data for furnace lots of ZIRLO tubes (approximately 21 inches) that were charged at 100, 200, 400, and 800 wppm H. Note that the hydrogen starts to absorb between 280 and 300°C.

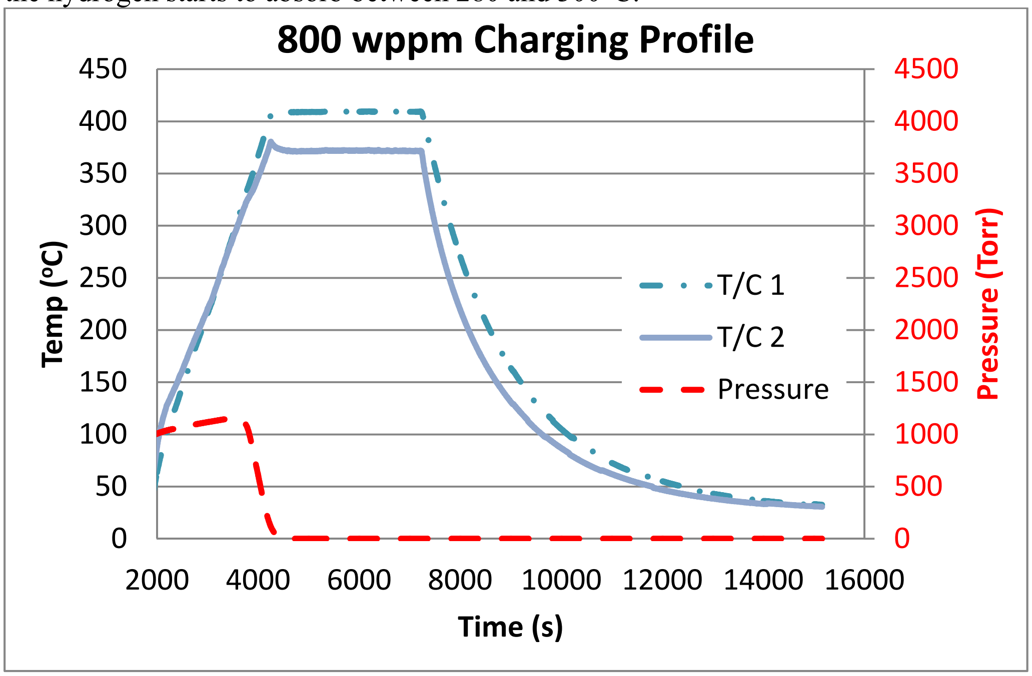


Figure 3. Typical absorption data for two ZIRLO samples charged with 800 wppm H in the same furnace load.

254 mm long samples were charged with 200 (Zr-10), 400 (Zr-11), and 800 (Zr-12) wppm H for chemical analysis. Each tube was cut into 19 samples that were 8 mm in length. Every other piece was chemically analyzed using inert gas fusion to determine the hydrogen content. The results from the hydrogen analyses are shown in Figure 5. As can be seen from the data from these three samples as hydrided condition, there is an axial profile of hydrogen content that varies with location and with nominal H content. The variation in H content changes from the nominal increases with increasing content. In addition to these three as-hydrided samples, one sample that had been charged to 800 wppm H (Zr-14) had also undergone RHGT at nominally 90 MPA, Figure 6 shows the thermal and pressure profiles.

In addition to the hydrogen content, the microstructure of the samples is important to determine the mechanical properties. The microstructure of 400 and 800 as-hydrided and RHGT samples are shown in Figure 7 for samples with 200, 400, 800 wppm. In reactor hydriding is typically characterized by the presence of a hydride rich structure on the external surface, a so-called rim structure. The samples in this study, in the as hydrided condition, did not exhibit an external rim structure, but rather an internal rim and nominally circumferential hydride precipitates. The morphology of the hydrides were modified after

RHGT. The extent of radial hydride formation is dependent on the H content as well as the stress level. The way that these samples were prepared results in a rim type structure on the internal diameter of the tube. This structure has been observed in other laboratory prepared samples, but is opposite of the hydride morphology observed in reactor exposed fuel cladding in which the outside diameter exhibits the rim structure due to oxidation and nascent hydriding. Additional characterization of the hydride morphology is possible for determining the extent of radial hydride formation, but this was not conducted on these samples. In general, the hydrides at the nominal 90 MPa hoop stress maintained a mostly circumferential orientation, while there are some hydride precipitates that are clearly in the radial orientation for the 200 wppm and 170 MPa. The extent of radial hydride reprecipitation being higher for the lower hydrogen content is consistent with the amount of hydrogen in solution. At the higher loading, there are more pre-existing hydrides for the soluble hydrogen atoms to precipitate and promote growth, rather than nucleating and growing new hydrides.

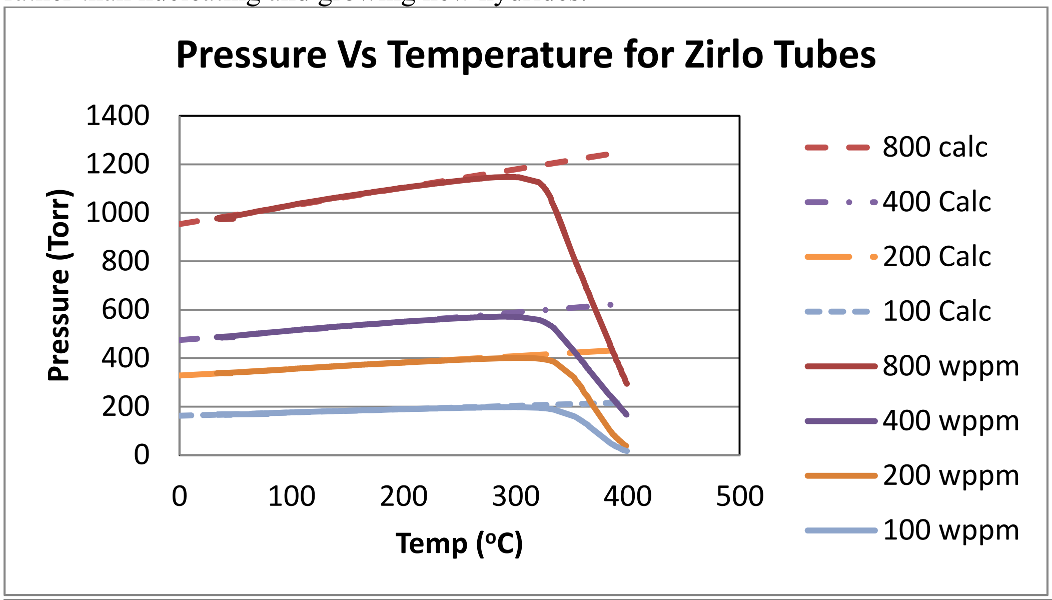


Figure 4. Thermal absorption data for samples charged with 100 to 800 wppm H using a common thermal profile.

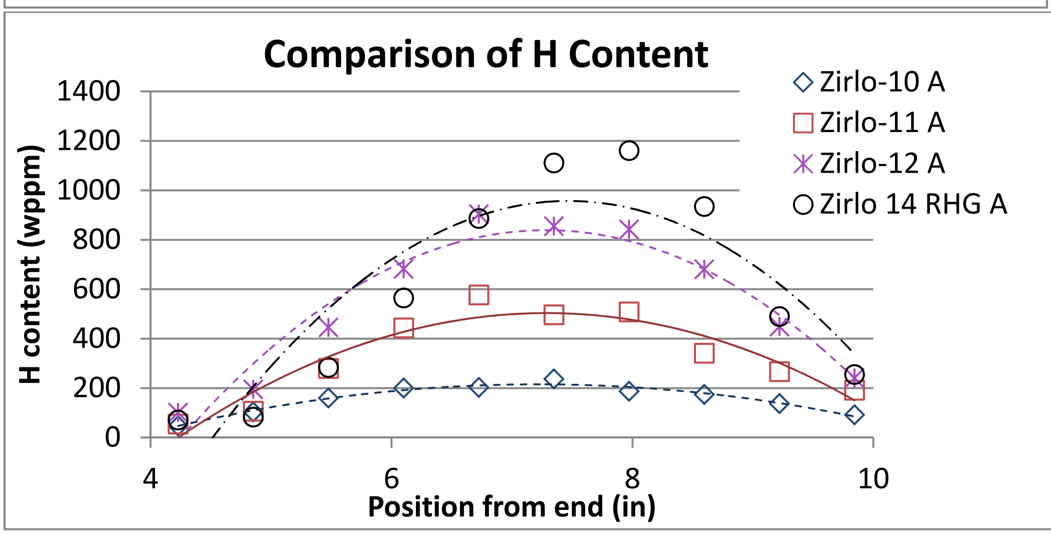


Figure 5. Hydrogen profiles as determined by inert gas fusion.

The ductile to brittle transition temperature (DBTT) was determined using both RCT and TPBT for samples with 800 wppm H. The samples exhibited cracking at 10.0 and 12.5% plastic strain (total displacement – elastic displacement) / ring diameter) for RCT. Samples that did not crack exhibited over 19% strain prior to test termination. The data from these tests are presented in Figure 8. The TPB test data are presented in Figure 9 for comparably conditioned samples. The estimated strain to first crack is 0.35% at 24°C, 0.42% at 75°C, 0.35% at 100°C, and greater than 0.42% for samples that did not fail,

$$e = \Delta * OD / L^2 \qquad \text{Eq. 1}$$

Where e is effective strain, OD is the outer diameter of the tube, and L is the span.

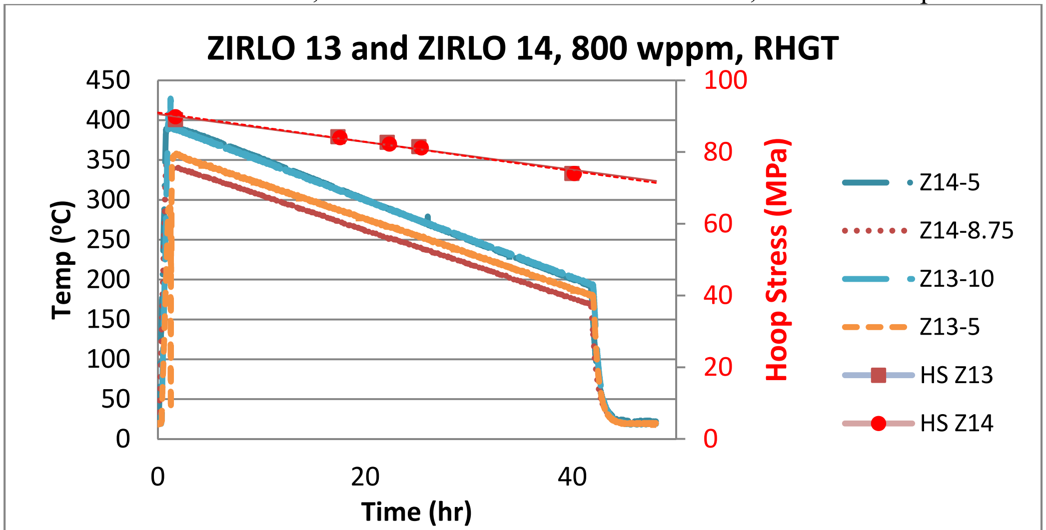


Figure 6. Thermal and pressure profile for a samples Zr-13 and Zr-14 loaded to 800 wppm H and subjected to RHGT at 90 MPa nominal hoop stress with a 5°C/hr cooling rate.

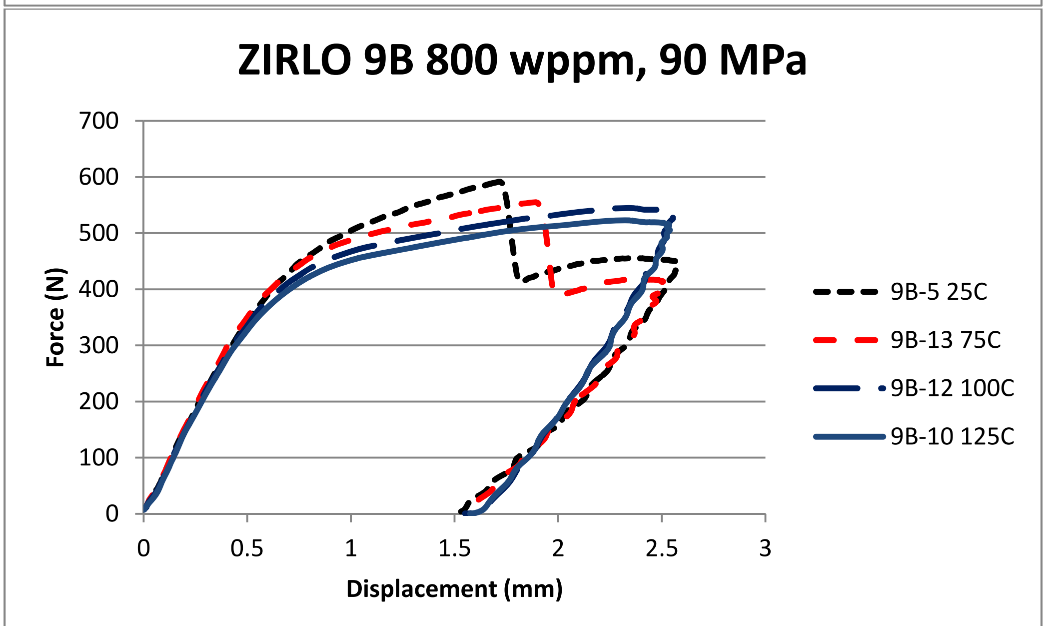


Figure 8. RCT data for a sample charged with 800 wppm H and subjected to a 90 MPa RHGT.

Summary

A method to charge and age ZIRLO tubing with suitable levels of hydrogen for DBTT testing was developed. Virtually all of the hydrogen charged to the tubes is absorbed on heating to 400°C. Samples subjected to a radial hydride growth treatment reveal that there are few radial hydrides formed at a 90 MPa hoop stress for a single thermal cycle at 800 wppm. There are some radial hydride observed at 130 MPa and even more radial hydrides at higher stresses. Lower hydrogen contents appear to generate more radial hydrides. The increased radial hydride versus circumferential hydrides ratio at the lower hydrogen levels is postulated to be a function of the solubility levels (most hydrogen is in solution) and the influence existing hydride structures have on reprecipitation hydrides (memory/lower activation - nucleation effect).

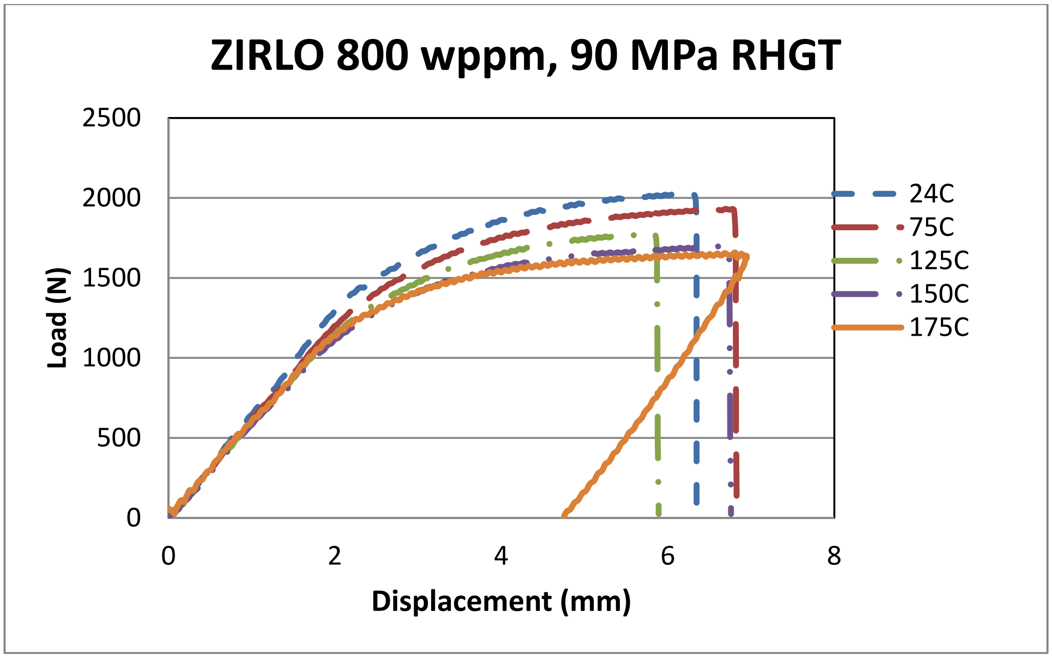


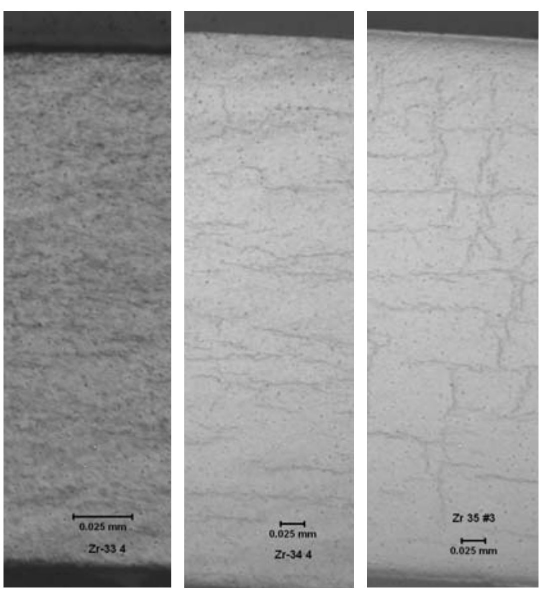
Figure 9. TPB test data showing the load deflection data for samples charged with 800 wppm H and subjected to a RHGT of 90 MPa hoop stress.

Acknowledgements

The authors would like to recognize Tony Curtis and Jacqueline Polz for their work on providing micrographs, Glenn Chapman for his efforts for the mechanical property testing, Savannah River National Laboratory for funding this activity as a Laboratory Directed Research and Development project, and the Department of Energy for funding this work under contract

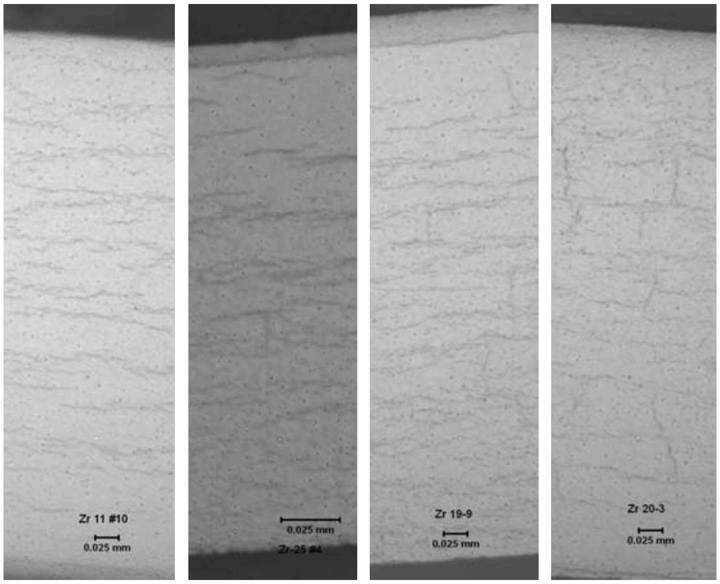
Figure 7 Metallographic cross-sections of samples with 200, 400, and 800 wppm in the as-hydrided and RHGT conditions.

200 wppm



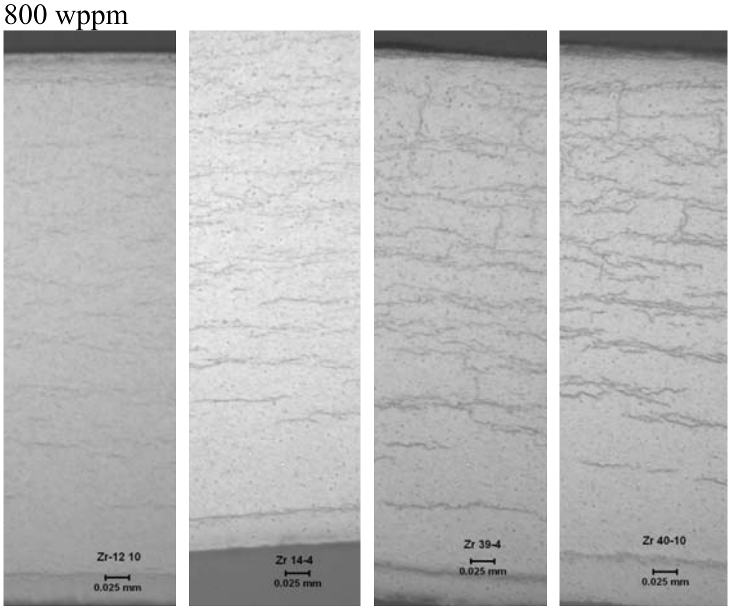
90 MPa 130 MPa 170 MPa

400 wppm



As Hydrided 90 MPa 130 MPa 170 MPa

800 wppm



As Hydrided 90 MPa 130 MPa 170 MPa

[1] MC Billone, TA Burtseva, RE Einziger "Ductile-to-brittle transition temperature for high-burnup cladding alloys exposed to simulated drying-storage conditions" JNM, 433 (2013) p 431-448)

[2] "The Adsorption of Hydrogen on Low Pressure Hydride Materials" Gregg A. Morgan, Jr.* and Paul S. Korinko, Conference Proceedings, Material Science and Technology 2011, October 16-20, 2011, COLUMBUS, OH