Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

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USED FUEL DISPOSITION CAMPAIGN

White Paper Summary of 2nd ASTM International Workshop on Hydrides in Zirconium Alloy Cladding

June 10-12, 2014
Jackson, WY

Fuel Cycle Research & Development

Prepared for
U.S. Department of Energy
Used Fuel Disposition Campaign

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May 29, 2015
FCRD-UFD-2015-000533
SRNL-STI-2015-00256

ABSTRACT

This white paper recommends that ASTM International develop standards to address the potential impact of hydrides on the long term performance of irradiated zirconium alloys. The need for such standards was apparent during the 2nd ASTM International Workshop on Hydrides in Zirconium Alloy Cladding and Assembly Components, sponsored by ASTM International Committee C26.13 and held on June 10-12, 2014, in Jackson, Wyoming. The potentially adverse impacts of hydrogen and hydrides on the long term performance of irradiated zirconium-alloy cladding on used fuel were shown to depend on multiple factors such as alloy chemistry and processing, irradiation and post irradiation history, residual and applied stresses and stress states, and the service environment. These factors determine the hydrogen content and hydride morphology in the alloy, which, in turn, influence the response of the alloy to the thermo-mechanical conditions imposed (and anticipated) during storage, transport and disposal of used nuclear fuel. Workshop presentations and discussions showed that although hydrogen/hydride induced degradation of zirconium alloys may be of concern, the potential for occurrence and the extent of anticipated degradation vary throughout the nuclear industry because of the variations in hydrogen content, hydride morphology, alloy chemistry and irradiation conditions. The tools and techniques used to characterize hydrides and hydride morphologies and their impacts on material performance also vary. Such variations make site-to-site comparisons of test results and observations difficult. There is no consensus that a single material or system characteristic (e.g., reactor type, burnup, hydrogen content, end-of life stress, alloy type, drying temperature, etc.) is an effective predictor of material response during long term storage or of performance after long term storage. Multi-variable correlations made for one alloy may not represent the behavior of another alloy exposed to identical conditions and the material responses to thermo-mechanical exposures will be different depending on the materials and systems used.

The discussions at the workshop showed several gaps in the standardization of processes and techniques necessary to assess the long term performance of irradiated zirconium alloy cladding during dry storage and transport. The development of, and adherence to, standards to help bridge these gaps will strengthen the technical basis for long term storage and post-storage operations, provide consistency across the nuclear industry, maximize the value of most observations, and enhance the understanding of behavioral differences among alloys. The need for, and potential benefits of, developing the recommended standards are illustrated in the various sections of this report.

1. Introduction

This report summarizes the presentations and discussions given to the 2^{nd} ASTM International Workshop on Hydrides in Zirconium Alloy Cladding and Assembly Components, sponsored by ASTM International Committee C26.13, held on June 10-12, 2014, in Jackson, Wyoming. The goal of the workshop was to initiate the development of international standards that drive toward a global position on the effects of hydrides on the long term performance of zirconium alloys associated with spent nuclear fuel and fuel assembly components. The need for this goal was confirmed by the participants and was apparent in the workshop presentations and discussions. Several standards and/or standard guides related to hydrides in zirconium alloys are recommended.

In this report, reference to specific presentations is made by listing the presenting author of the presentation. For example (Adamson) refers to Ron Adamson's presentation "Hydrogen and Hydrides in Zr-Alloys – a review." Presentation titles and presenting authors included:

1)	Welcome and Workshop Agenda	Brady Hanson, PNNL
2)	Issues from a Regulatory Perspective	Bob Einziger, USNRC
3)	Old Data and New Knowledge	Mac Louthan, SRNL
4)	Performance Considerations for Used BWR Fuel in Dry Storage and Transportation	Randy Dunavant, GE– GNF
5)	Hydrogen and Hydrides in Zr – Alloys A Review	R. B. Adamson, Zircaloy Plus
6)	Hydride Dissolution and Precipitation in Zirconium Based Alloys (Licensing and Field Conditions)	A. J. Machiels, EPRI
7)	Characterization Techniques to Quantify Hydrogen Content, Hydride Morphology and Orientation on Unirradiated and Irradiated Zirconium Alloy Cladding	K. Colas, CEA-Saclay
8)	Laboratory Reproduction of the Different Hydride Morphologies in Non-Irradiated Zirconium Alloy Cladding	J. Ruiz-Hervias, Technical University of Madrid
9)	Hydriding of Unirradiated Samples	R. Shimskey, PNNL
10)	The Perils and Pitfalls of Applying Hydrides Characterization Experiments to Cladding Performance In-Reactor and Backend Fuel Cycle	J. Rashid, ANATECH-SIA
11)	Experimental Study of Embrittlement of As-Hydrided and Hydride Reoriented Zry-4 Cladding	Y. Yan, ORNL
12)	PNNL Baseline (As-received)Testing	C. Lavender, PNNL
13)	End-of-Life Internal Pressures for High-Burnup PWR Fuel Rods	M. C. Billone, ANL
14)	Effect of Stress State on Hydride Reorientation in Zirconium Alloys	A. T. Motta, Penn State
15)	Spent Nuclear Fuel Behavior Under Dry Transportation and Storage (Impact of Radial Hydride Precipitation on the Mechanical Strength of Unirradiated CWSR Zircaloy-4)	N. Mozzani, EDF, France

16)	DBTT for High-Burnup PWR Fuel- Cladding Alloys	M. C. Billone, ANL
17)	Comparison of Ductile to Brittle Transition Testing Method for Used Nuclear Fuel (or ZIRLO Hydrogen Charging, Reorienting, and Testing)	Paul Korinko, SRNL
18)	The Recent Development on Investigation Spent Fuel Vibratory Reliability under Normal Transport Vibration	J-A. Wang, ORNL
19)	Effect of Hydriding on the Creep of HANA 4 Zircaloy	Jacob Eapen, NCSU
20)	Nondestructive Study of Hydrided Zry-4 by Neutron Incoherent Scattering of Hydrogen	Y. Yan, ORNL
21)	Modeling and Simulation of Hydrogen Transport in Zircaloy-4 Fuel Cladding under Temperature and Concentration Gradients	A. T. Motta, Penn State
22)	Simulation of Hydride Precipitation in Zircaloy-4 Cladding During Dry Storage	V. Tikare, SNL
23)	Wrap Up and Path Forward	Brady Hanson, PNNL

Electronic copies of the slides used for 20 of the 23 listed presentations have been reviewed (no copies for presentations 2, 18 and 22) and the slide packages may be available from the presenter. All 23 presentations were combined with the Workshop discussions to develop this summary document and all participants contributed to the success of the Workshop.

This report fulfills UFD ST-Experiments milestone M3FT-15SR0805061, *Issue white paper on "Hydrides in Zirconium Alloy Cladding and Assembly Components."*

2. Technical Summary of Presentations and Discussion

The extant literature on hydrogen and hydrides in zirconium alloys is so extensive that it is almost overwhelming. Zirconium alloys have been successfully used, worldwide, in virtually all water cooled nuclear power reactors for fifty plus years. Nuclear grade zirconium alloys typically contain at least 95% zirconium with small additions of niobium, tin, nickel and/or chromium. The alloy elements are generally added to improve the mechanical properties and corrosion resistance but may also alter material performance in other arenas. The coolant temperatures, chemistry and pressures to which the claddings are exposed vary with reactor type and, over the years, a wide variety of alloy claddings have been used. It is basically unreasonable to expect similar behaviors among the wide variety of cladding alloys. The International Atomic Energy Agency has published extensive reviews of alloy performance under various laboratory and in-reactor environments. The data and analyses presented at the workshop are consistent with the literature and demonstrate a need for international standards as a precursor to the development of a global position on the effects of hydrogen and hydrides on the long term performance of zirconium alloy claddings on used nuclear fuels.

Corrosion of zirconium alloy claddings on nuclear fuels during reactor service results in the formation and growth of an oxide film on outer cladding surface and the absorption of some of the hydrogen generated during the corrosion processes. The bulk of the hydrogen, however, is released to the cooling water and only a fraction of the generated hydrogen is absorbed (Adamson). The magnitude of this fraction varies from about 5% to over 50% depending on alloy type and reactor operating conditions. The corrosion reaction is basically:

$$Zr + 2H_2O \rightarrow ZrO_2 + 4H.$$

The absorbed hydrogen, depending on the temperature and the amount of hydrogen absorbed, may remain in solid solution in the zirconium lattice or precipitate as a hydride (Yan). Transmission electron microscopy demonstrates that the basal or (0001) planes in the zirconium alloy matrix are the dominant hydride habit plane (Tikare). Optical microscopy indications of other habit planes often result from the analysis of the orientation of a stack of very small basal plane hydrides that are not generally resolved by optical microscopy (Tikare and Colas). Many of the long hydrides seen in etched samples are actually stacks of adjacent, very short segments (Adamson, Colas). The precipitation of one hydride segment apparently lowers the activation or accommodation energy (the mechanical work required to form a hydride precipitate in the solid) required for hydride nucleation in areas adjacent to the existing hydride. This lowering of the energy required for hydride nucleation makes the stacking of short hydride segments favorable. The hydride stacks frequently appear, in optical metallography, as long hydrides having an apparent orientation that differs from the orientation of the individual hydride segments. Hydrides also may precipitate along grain boundaries, twin boundaries and in association with other lattice defects.

The orientation and continuity of the long hydrides play major roles in determining the mechanical response of the alloy to applied and residual stresses. Characterization of hydride morphology is therefore critical to determining (and predicting) the effects of hydrides on the behavior of used fuels during long term storage and post-storage transfer (handling, transportation and disposition).

Optical microscopy is generally used to characterize the hydride microstructure in irradiated and non-irradiated fuel cladding. The metallographic preparation generally includes grinding, polishing and etching the surface of a mounted cross section of the material of interest. Etching makes the hydrides observable in the optical microscope (typically 25 to 500X magnification) by: 1) removing the smeared surface layer that developed during polishing, and 2) chemically attacking the hydrides, the metal and the hydride/metal interface region at different rates. The quality of the image and the appearance of the hydrides are very sensitive to the metallographic preparation practices. This sensitivity may result in image differences even when the hydrogen content of the samples is very similar. The image differences in the three micrographs shown in Figure 1 are primarily the result of site-to-site differences in metallographic preparation techniques even though different alloys are shown. All three samples contain oriented hydrides but the apparent width of the hydrides and the resolution of detail among long hydrides differ significantly.

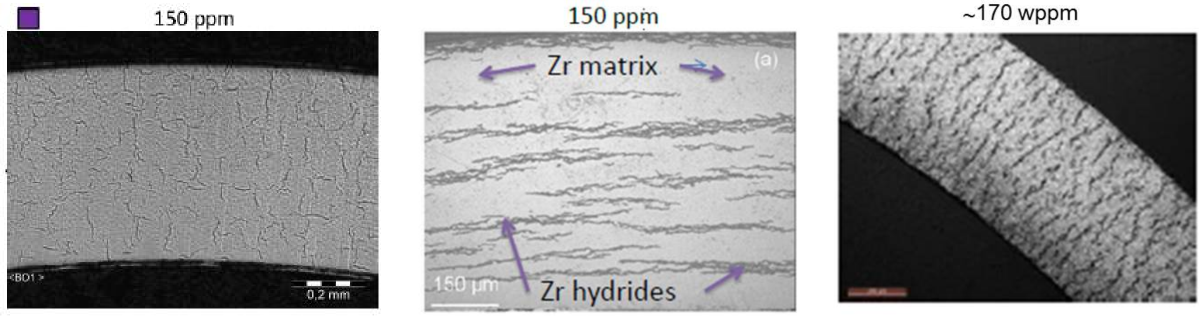


Figure 1a
(Presentation 15, Slide 14)

Figure 1b
(Presentation 8, Slide 7)

Figure 1c
(Presentation 11, Slide 11)

Figure 1: Optical Micrographs of Several Zirconium Alloys Containing Similar Amounts of Hydrogen.

1a) is a non-irradiated CWSR Zry-4 with 150 ppm hydrogen after a hydride reorientation treatment; **1b)** is an as-hydrided ZIRLO alloy that contained 150 ppm hydrogen; and **1c)** is a non-irradiated Zry-4 alloy that contained 170 ppm hydrogen and had experienced a hydride reorientation treatment. Note the apparent differences in the hydrides and the apparent volume fraction hydrides in the samples.

As shown Figure 1, image differences among similar materials prepared by different metallographic practices illustrate the need for standardized or at least uniform metallographic preparation procedures. Creating a well prepared metallographic image often involves artistic renderings which are difficult to standardize; however, efforts should be made to recommend metallographic practices to assure that the apparent hydride fraction in the image actually represents the hydride fraction in the alloy.

Hydride precipitation in zirconium alloys in nuclear fuel cladding generally involves a sequence of steps that result in the formation of δ-hydrides ($ZrH_{1.59}$). The density of the δ-hydride is significantly less than the density of zirconium. Hydride nucleation is accompanied by a local lattice expansion, and to accommodate the expansion dislocation loops are created in the matrix. The necessity of dislocation nucleation during hydride precipitation provides an energy barrier that must be overcome before precipitation can occur (IAEA – TECDOC-1410). This is not the case for hydride dissolution; thus there is a hysteresis in the solubility versus temperature curve as indicated in Figure 2 for non-irradiated Zr-2 and -4 samples in the annealed and cold worked conditions.

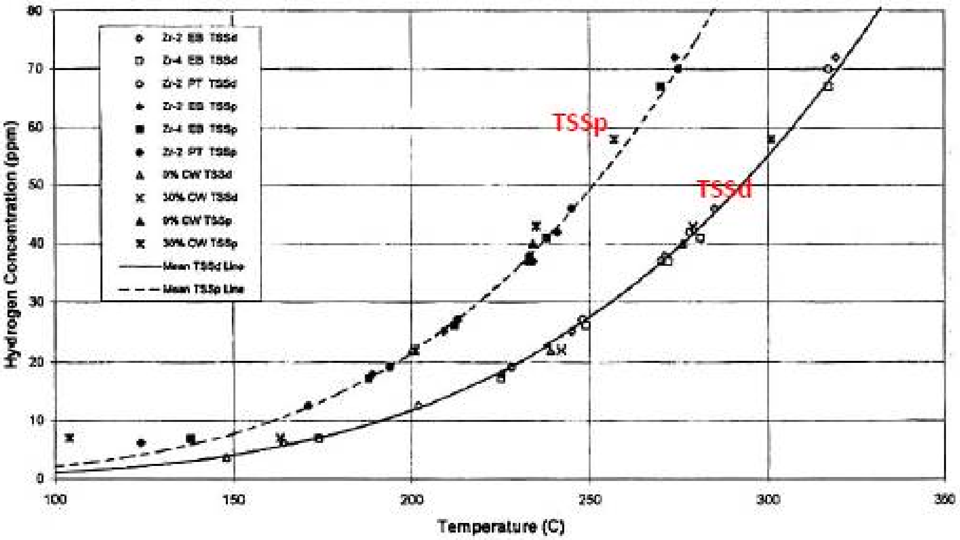


Figure 2: Terminal Solubility of Hydrogen in Zircaloy Alloys as Detected by the Onset of Hydride Precipitation (TSSp) during Cooling from Elevated Temperatures and as Detected by Hydride Dissolution (TSSd) during Heating from Low Temperatures. (Presentation 5, Slide 4)

This figure suggests that, for example, Zry-4 cladding containing 50 ppm hydrogen at room temperature must be heated to approximately 563K (290°C) to dissolve all the hydrides and after the hydrides have been dissolved the sample must be cooled to 523K (250°C) before the hydride re-precipitation begins. However, if the sample were only heated to 548K (275°C), some hydrides would remain in the microstructure and, as observed by K. Colas in a hydride reorientation experiment in which a sample containing excess hydrides was used (Presentation 7) and the initiation of hydride re-precipitation and/or the growth of existing hydrides could begin immediately upon cooling. Re-precipitation is easier when hydrides are present because, as previously discussed, a hydride segment can lower the accommodation energy required for hydride nucleation in areas adjacent to the existing hydride.

Irradiation apparently increases the hydrogen solubility (Figure 3) although this increase is minimized or eliminated if the irradiated material is annealed at 673K (400°C) or higher. These observations give support to the hypothesized interaction between irradiation defects and hydrogen as the cause of the apparent solubility increase when the solubility is inferred using differential scanning calorimetry. Annealing may also dissolve some (or all) of the precipitated hydrides depending on the hydrogen concentration in the alloy. But even if all the hydride is dissolved, a local dislocation structure (a dislocation loop structure or nest) produced during hydride precipitation may act as a favored site for hydride nucleation and alter precipitation kinetics.

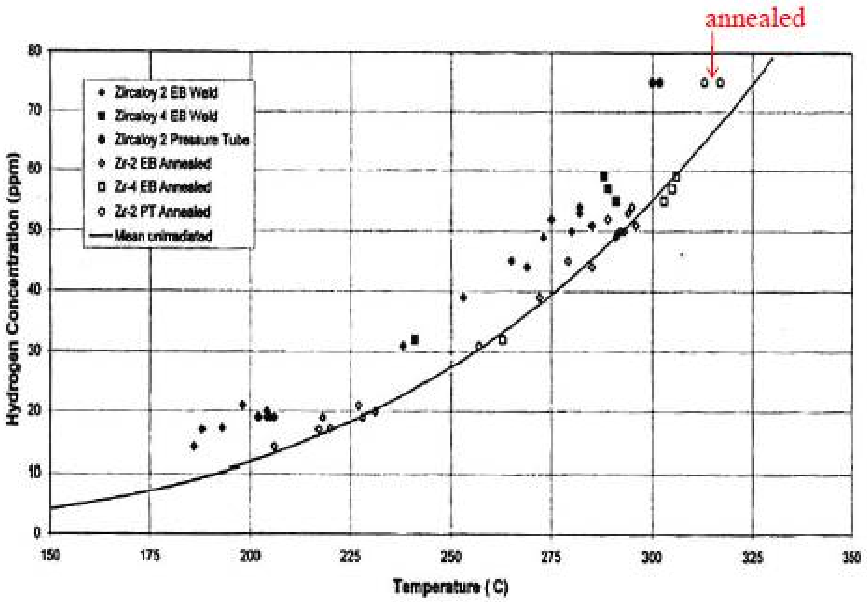


Figure 3: TSSd for Irradiated Zircaloy Samples compared to the Non-Irradiated Mean Line. (Presentation 5, Slide 6)

The presence of a punched loop or dislocation nest coupled with the tendency for hydride nucleation in areas adjacent to existing hydrides may give an alloy a “memory effect” which will influence subsequent hydride precipitation, especially if all the hydrides were not dissolved during the heating cycle. In the latter case, i.e., incomplete dissolution, the memory effect is sometimes referred to as “sympathetic nucleation.” Some authors make the distinction between “memory effect” (which, in this case, assumes complete hydride dissolution) and “sympathetic nucleation” (which, in this case, assumes incomplete hydride dissolution).

The solubility of hydrogen in the metal lattice is, as a first approximation, alloy-independent for cladding materials (Adamson) even though pure zirconium has a lower solubility than any of the alloys. This lower solubility in pure zirconium can result the liner of a barrier cladding becoming a hydrogen sink that causes hydrogen to concentrate in the inner zirconium layer. This tendency for hydrogen segregation to the barrier layer is evident in Figure 4, which also illustrates the importance of cooling rate on hydride distribution in irradiated claddings and the need to treat the lined claddings for BWR’s differently than non-lined PWR cladding alloys. Diffusion of hydrogen followed by precipitation of hydrogen into the barrier layer creates a hydride-depleted zone adjacent to the inner liner. This hydride-depleted zone acts as a mitigating factor against hydrogen-induced degradation processes in the lined cladding.

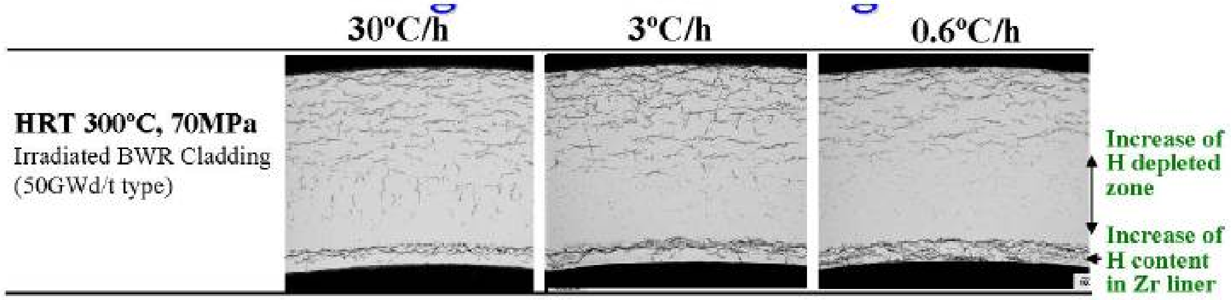
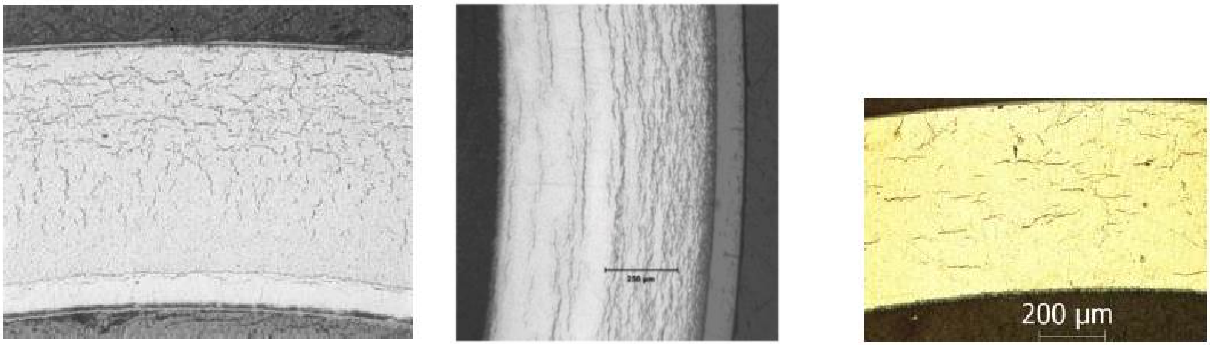


Figure 4: Hydrogen Segregation to the Pure Zirconium Layer in BWR Barrier Cladding and the Effect of Cooling Rate on the Segregation Process. The irradiated samples were heated to 573K and cooled to room temperature at the rates shown. (Presentation 4, Slide 6)

The mechanical and fracture properties of the zirconium alloys are affected by hydride precipitation and the degree of the effect depends on the hydride morphology. The morphologies depend on thermal and stress gradients acting on the materials (Motta, Ruiz Hervias) as well as the thermo-mechanical history of the material and the alloy being tested (Billone). The hydride distributions are not homogeneous (Motta) and, in the cladding of a single fuel rod, vary in the longitudinal, circumferential and axial directions. The microstructure developed after any given exposure or fuel burnup is both reactor operation and fuel cladding dependent, as demonstrated in Figure 5, which compares the claddings on high burnup fuels from a BWR and two PWR reactors.



5a) BWR Barrier Fuel (Presentation 4, Slide 5)

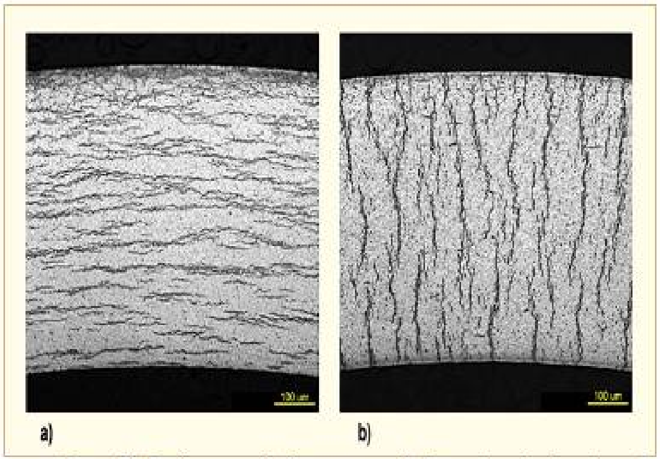
5b) Zr-4 Cladding from PWR Fuel (Presentation 10, Slide 3)

5c) M5 Cladding from PWR Fuel (Presentation 16, Slide 11)

Figure 5: Room Temperature Microstructures in As-Irradiated High Burnup Fuel Claddings. 5a) is a BWR barrier fuel cladding that contains 173 ppm hydrogen after irradiation to 52.7 GWd/MTU, 5b) is a Zr-4 cladding from a PWR fuel that contains 320 ppm hydrogen after irradiation to 47 GWd/MTU, and 5c) is an M5 cladding from a high burnup fuel that contains 76 ppm hydrogen.

The obvious differences in oxide film thicknesses, hydrogen content and hydride distribution and orientation in the claddings shown in Figure 5 demonstrate the wide range of microstructures developed in fuel cladding irradiated to high burnups. These differences in microstructure coupled with differences in crystallographic texture, susceptibility to stress orientation, end-of-life internal pressures and other fuel/cladding variables complicate the development of reasonably accurate predictions of cladding response during drying and storage. The metallographic differences shown in Figure 5, support the need for standardization of fuel/cladding characterization technologies in order to strengthen the technical and scientific basis for predicting the behavior of hydrogen in zirconium alloys during extended storage and post-storage operations. It is simply inadequate to discuss “high burnup fuels” or PWR claddings as a single group for technical or scientific purposes.

Fuel claddings are fabricated so that hydrides preferentially precipitate in a circumferential orientation when the hydrogen concentration in the alloy exceeds its solubility limit in the reactor. However, depending on the tube fabrication process, hydrides may orient radially in the cladding when precipitation occurs while a sufficiently large hoop stress acts on the fuel tube. This stress-induced reorientation process, an extreme example of which is shown in Figure 6, drastically reduces the ductility of the alloy and may lead to hydrogen embrittlement (Adamson), delayed hydride cracking (Dunavant) and/or an increase in the ductile-to-brittle transformation temperature (Billone).



circumferential (tangential) radial, reoriented under stress

Figure 6: Stress Orientation of Hydrides in Cladding. Note that the circumferential, as-hydrided microstructure became radial when the sample was heated, to a high enough temperature to dissolve all the hydrides, and then cooled to room temperature under a hoop stress sufficiently large to re-orient all the hydrides. (Presentation 5, Slide 11)

The susceptibility to radial hydride precipitation varies from alloy to alloy. In high burnup fuel claddings, the susceptibility to stress orientation is low for CWSR Zry-4, moderate for CWSR ZIRLO™ and high for RXA M5® (Billone). Additionally, the tendency for radial hydride precipitation depends on the stress acting on the cladding (Motta), hydrogen content in the cladding (Ruiz Hervias) and the cooling rate during hydride precipitation (Dunavant). The tendency for radial hydride precipitation also depends on the cladding alloy microstructure (SRA-RXA), existing hydride morphology and rim effects and the number of temperature cycles experienced by the alloy. Additionally, there is not a one to one correspondence between the susceptibility of an alloy to radial hydride precipitation and the mechanical response of the alloy (loss of ductility for example) after stress orientation or hydride reorientation.

The response of the cladding to stresses imposed during a mechanical test is influenced by alloy chemistry, hydrogen content and distribution, hydride orientation and continuity, the rate of load application, the test technique and the test temperature. Non-irradiated materials tested to determine the impact of hydrogen and hydrides on nuclear fuel cladding often contained relatively uniform hydrogen distributions compared to the non-uniform distributions generally found in irradiated claddings (Figure 7). This potential difference in hydrogen morphologies is one reason tests results for non-irradiated alloys may differ significantly from the results from irradiated alloys containing similar hydrogen concentrations. Therefore, hydriding techniques to produce hydride blisters, rims and other regions of hydride localization have been developed (Ruiz Heriava, Shimskey, Korinko).

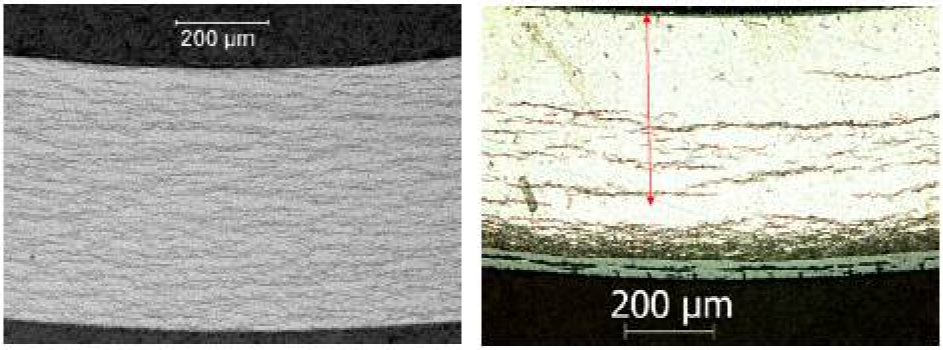


Figure 7: Uniform Hydrogen/Hydride Distributions Often Used for Testing Non-Irradiated Materials Compared to the Non-Uniform Distributions Typical of Irradiated Alloys (Presentation 9, Slide 4)

The terms hydride rim and hydride blister are qualitative terms that need to be given more precise/quantitative definitions to be compatible with the precisionist nature of an ASTM standard. The following definitions are suggested:

"A **hydride rim** is defined as a narrow zone at the cladding outer surface (metal-oxide interface) having a radially increasing density of circumferential hydrides, with a hydrogen concentrations in the rim that is ≥ 1200 ppm." The reason for choosing the 1200 ppm value as the metric for characterizing the "**hydride rim**" is that the tensile capacity of a cladding with such hydride concentration is so small that it can be totally ignored vis-à-vis the cladding mechanical resistance.

"A **hydride blister** is defined as a volume of densely hydrided cladding, with nearly δ-hydride concentration (16,600 ppm) that resulted from intense hydrogen localization." For example, blisters have developed by a process involving, first, the formation of a thick oxide in Zr-4 cladding, which increased the temperature of the cladding at the metal/oxide interface. The oxide then delaminated and spalled from the cladding exposing the underlying metal to the coolant producing a locally steep temperature gradient and a deep hydrogen sink.

An example of a non-irradiated cladding alloy containing a carefully produced hydride rim is shown in Figure 8. Unfortunately, many tests with non-irradiated alloys failed to use test samples that were hydrided to produce microstructures similar to those found in irradiated claddings.

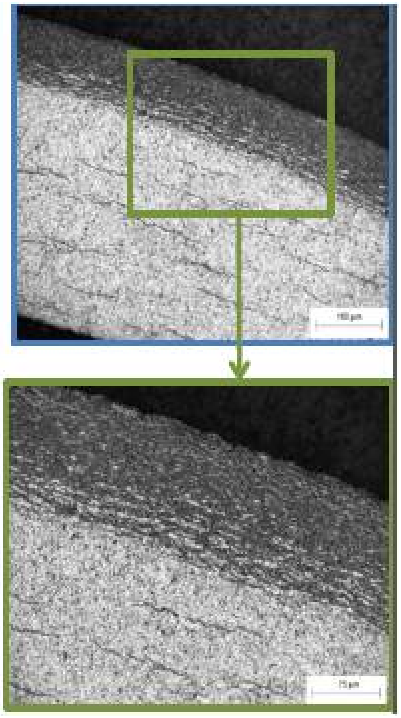


Figure 8: A Hydride Rim on a Non-Irradiated Zry-4 Cladding Alloy Hydrided by Exposure to Hydrogen Gas at 563K (Presentation 9, Slide 15)

The regions of locally high hydrogen contents typically produced in irradiated fuel claddings are similar to that shown in Figure 8. However, the hydride morphology developed in any given cladding depends on the reactor system and cladding alloy (see Figure 5 for example) as well as fuel burnup and post irradiation thermal history. Simulating the hydride morphology developed in irradiated cladding alloys in non-irradiated test materials is critical to developing meaningful test protocols for non-irradiated alloys. In fact, the results of tests on non-irradiated alloys that do not contain hydride morphologies that simulate irradiated material microstructures are likely to be irrelevant, at best, and may even be misleading.

The thermodynamic properties of the zirconium-hydrogen system are such that hydrogen tends to segregate to regions of lattice dilation and migrate toward the cold region of a thermal gradient. These tendencies coupled with the absorption of corrosion-produced hydrogen from the outer cladding surface create hydride morphologies on irradiated claddings similar to those shown in Figure 5. Thermal cycling, such as may be encountered during drying of a used fuel assembly for long term dry storage, may alter the hydride morphology. The heat involved with the drying process, Figure 9, locally increases the cladding temperature, which results in an increase in hydrogen solubility in the cladding, and may partially or completely dissolve any hydrides that precipitated when the fuel was removed from the reactor and placed in pool storage. The dissolved hydrogen progressively re-precipitates as the dried fuel cools over time. The orientation of the precipitating hydrides is strongly influenced by stresses acting on the cladding, the cooling rate and the presence of non-dissolved hydrides.

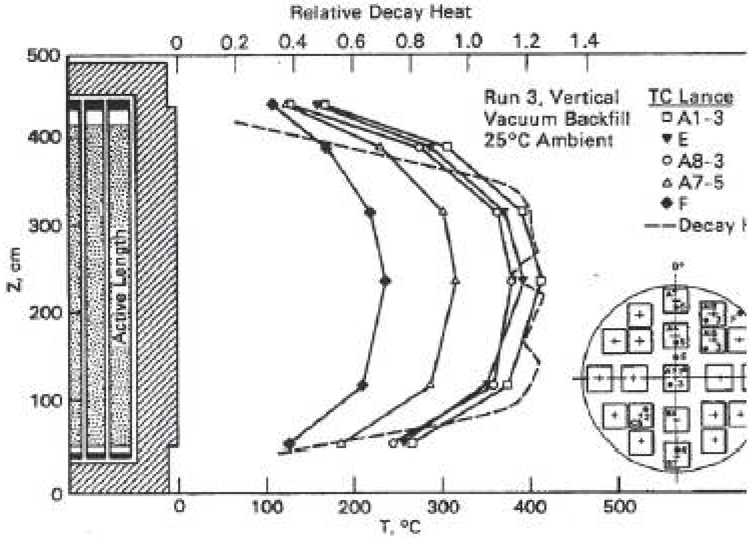


Figure 9: Measured Axial Temperature Profiles Developed during a Vertical Vacuum Test Drying of Used Fuel (Presentation 6, Slide 6)

The importance of stress on hydride reorientation is illustrated in Figure 10 which shows the reorientation of hydrides in a non-irradiated, tapered tensile sample containing 150 ppm hydrogen. The sample was heated to 773K to dissolve the hydrides, loaded to produce the stresses shown in Figure 10, and then cooled to room temperature to re-precipitate the hydrides. It is important to recognize that the magnitude of stress dependent transitions in hydride orientations seen in Figure 10 may bear little or no relationship to the magnitude of stresses requires for hydride reorientation in other alloys or in irradiated materials.

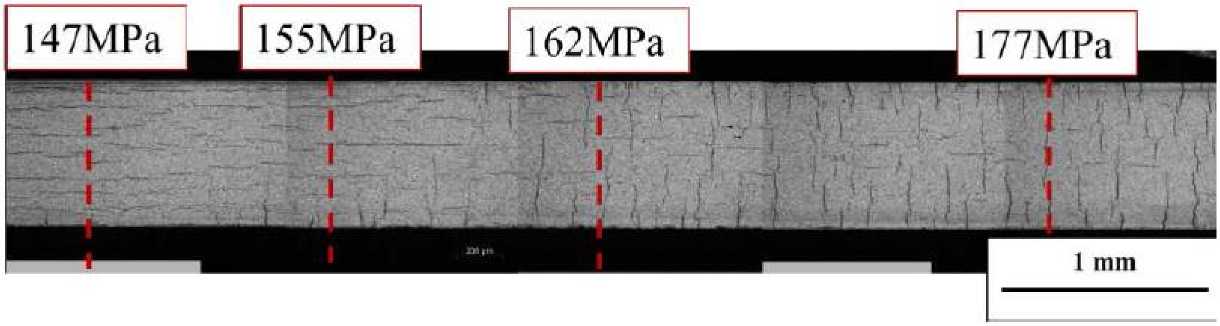


Figure 10: Hydride Reorientation in a Tapered CW-SRA Zry-4 Tensile Sample Heated to 773K and Cooled to Room Temperature under Stress (Presentation 14, Slide 15)

The hydride dissolution-reprecipitation process is a thermal treatment often identified either as: 1) a radial hydride treatment (RHT); 2) a radial hydride growth treatment (RHGT); or 3) a hydride reorientation treatment (HRO). All three identifications were used during the workshop. The change in hydride morphology associated with a thermal treatment depends on the hydrogen content in the cladding, the maximum temperature obtained during the thermal treatment, the hoop stress acting on the cladding during hydride precipitation, the memory effect associated with prior hydride precipitation, the type of cladding, the cooling rate during hydride precipitation, grain structure, and temperature differentials . An example of the evolution of cladding microstructure is shown in Figure 11.

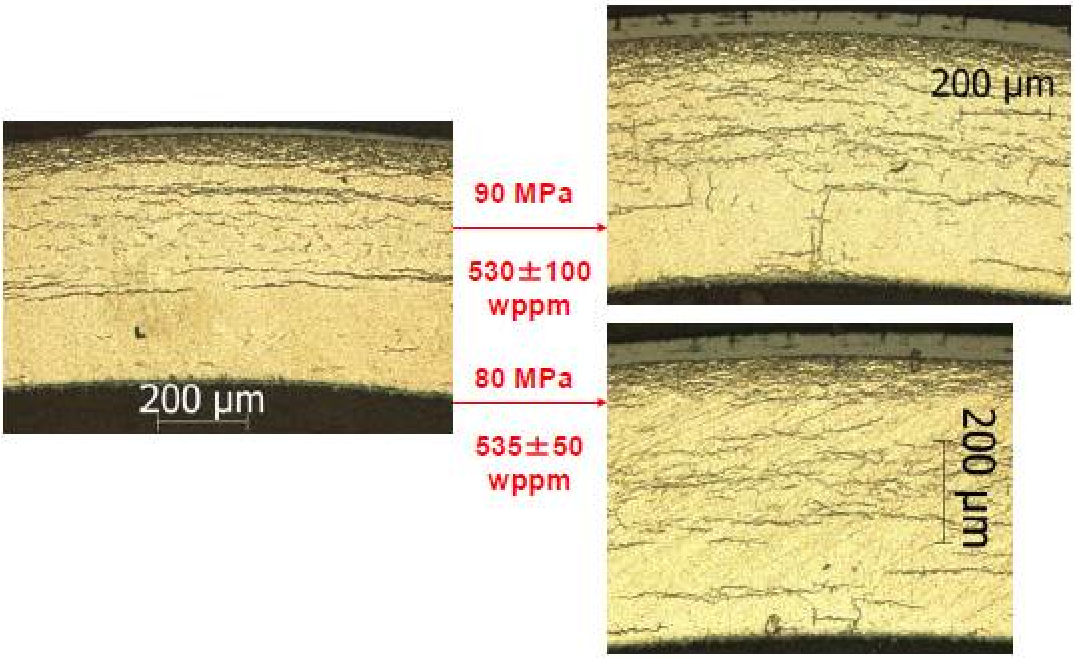


Figure 11: Hydride Reorientation in Irradiated ZIRLO Cladding Heated to 673K and Cooled under Stress (Presentation 16, Slide 16)

The long hydrides, which were primarily circumferential in the baseline, as-irradiated ZIRLO cladding that contained over 500 ppm hydrogen, became more radial during the RHT. Additionally, the tendency for radial hydrides was higher when the applied hoop stress was 90 MPa than when the hoop stress was 80 MPa, and the hydride distribution across the cladding wall became more uniform because of diffusion during the RHT. It is possible that the differences between two stressed samples simply result from microstructural inhomogeneity. However, the hydride reorientation during a RHT of sections of irradiated M5 cladding that contained less than 100 ppm hydrogen is clearly the result of the stress acting on the alloy during hydride precipitation (Figure 12).

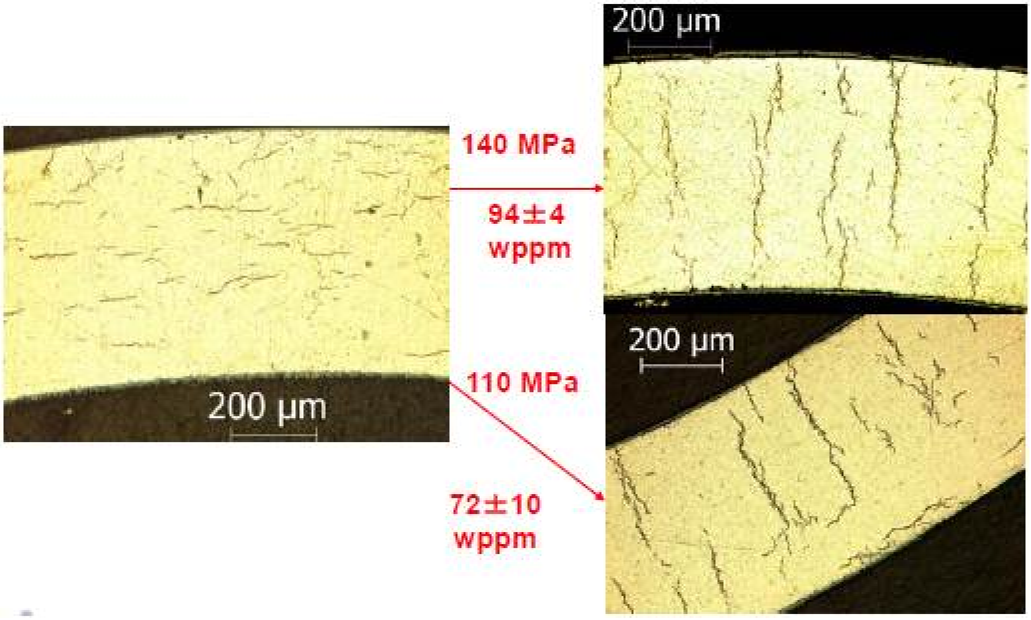


Figure 12: Hydride Reorientation in Irradiated M5 Cladding Heated to 673K and Cooled Under Stress (Presentation 16, Slide 11)

The RHT of both the ZIRLO and M5 claddings involved heating to 673K and cooling. This treatment dissolved all the hydrides in the M5 cladding while less than half of the hydrides in the ZIRLO cladding were dissolved. The undissolved hydrides that remained in the ZIRLO cladding sections during the RHT influenced subsequent hydride precipitation and may have partially inhibited the stress orientation process. Similar observations were made on non-irradiated cladding samples (Ruiz Hervias). These observations point out the necessity of knowing whether the amount of hydrogen available was above or below the solubility limit when interpreting a reorientation metric. For RCT type testing with hoop stresses, the precipitation of long apparently radial hydrides (actually radial stacks of hydrides) may significantly reduce the ductility of the cladding and lead to brittle fracture as illustrated in the irradiated M5 cladding section shown in Figure 13. It should be noted that the cladding is not isotropic and that the RCT ductility will be affected by radial hydrides while the axial ductility will be less affected. This is important to consider when evaluating potential accident conditions and failure modes.

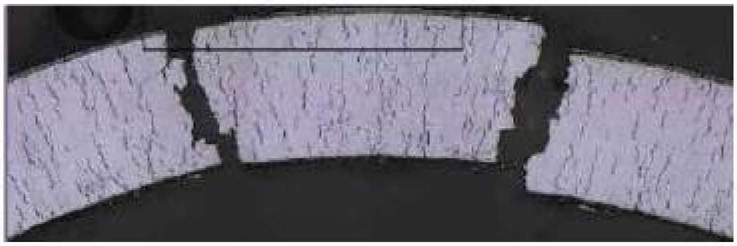


Figure 13: Brittle Fracture in Irradiated M5 Cladding after Creep Testing and Hydride Reorientation (Presentation 7, Slide 2)

Hydride dissolution and reprecipitation in the cladding of used fuel being transferred from pool to dry storage and during the long time intervals associated with dry storage may degrade the mechanical properties of the cladding. Such degradation could include embrittlement and/or delayed hydride cracking. Additionally, the very slow cooling rates associated with dry storage may lead to hydride precipitation processes that couple with the end-of-life cladding stresses to cause hydride reorientation and cladding degradation. The magnitude of the hoop stress acting on the cladding during hydride precipitation (reprecipitation) will significantly impact the hydride reorientation process. As illustrated in Figure 10, there is a threshold stress necessary to cause hydride reorientation. However, a single value for the threshold hydride reorientation stress in zirconium alloys does not exist and apparent values vary with alloy chemistry, irradiation and thermo-mechanical history, cooling rates and other material/system variables. In fact, the threshold stress in any given cladding is anisotropic and differs significantly in the longitudinal and circumferential directions. The influence of material/system variables on the reorientation process makes predicting a threshold hydride reorientation stress difficult. For example, the impact of thermal cycling on hydride reorientation may be difference in the HBU fuel loaded and stored on site for some extended time period verse HBU fuel immediately transported without extended cooling because of the differences in thermo-mechanical history. However, regardless of the specific value of the threshold stress for hydride reorientation, the stress acting on the cladding during hydride precipitation will be important and, if reorientation occurs, could lead to embrittlement and/or delayed hydride cracking.

Creep, which is often considered a potential degradation mechanism, can actually have a dampening effect on radial hydrides precipitation in fuel rods because of the decaying hoop stress caused by the pressure reduction due to the expansion of the fuel-cladding gap. Determinations of the end-of-life cladding stresses in ZIRLO-clad, high burnup PWR fuel rods suggest that at 673K a hoop stress as high as 90 MPa may be developed (Billone). Such stresses may or may not exceed the threshold stress, depending on cladding alloy and service history.

Stress state also impacts the threshold stress for hydride reorientation, Figure 14 (Motta). Most determinations of threshold stresses for hydride reorientation have been made under near uniaxial test conditions, thus, most reported threshold stress values may not be applicable to reorientation in a closed fuel rod. The hoop stress in a closed fuel rod is associated with a biaxiality ratio of 0.5, and assuming that the effect of biaxiality on hydride reorientation in fuel cladding is qualitatively similar to that in the sheet material depicted in Figure 14 the threshold stress, as calculated from a normalized form of Figure 14, would be approximately 27% lower in a closed tube than in an open tube. However, this has to remain as an un-verified information until a hydride reorientation test is performed using a closed tube subjected to axial compression to simulate open tube reorientation test.

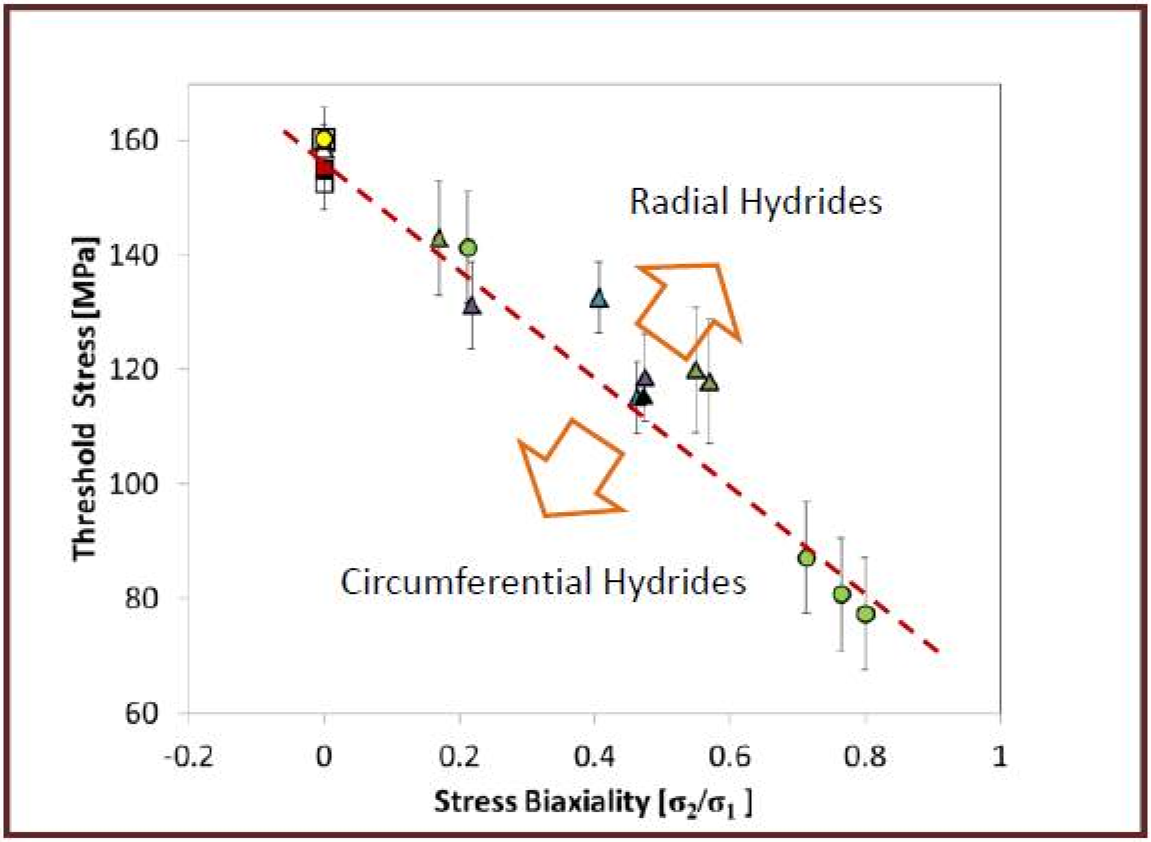


Figure 14: Effect of Stress Biaxiality on the Threshold Stress for Hydride Reorientation in Zircaloy-4 Sheet Material (Presentation 14, Slide 27)

Variations in apparent threshold stress values were apparent from the workshop presentations. Tests on non-irradiated CWSR Zircaloy-4 tube material showed that the threshold stress for radial hydride formation was 70 MPa (Mozzani) while tests with irradiated Zry-2 showed hydride reorientation at stresses as low as 28 MPa (Adamson). The differences in these threshold stresses illustrate the importance of irradiation, alloy chemistry, stress state and fabrication process on hydride reorientation. Alloy-to-alloy differences in mechanical behavior were also illustrated by creep data which showed that hydrogen in solution decreased creep rates in CWSR Zircaloy-4 (Mozzani) but increased creep rates in HANA 4 cladding (Eapen). Precipitated hydrides decreased the creep rates in both alloys.

Quantitative determinations of the extent of reorientation are generally made through optical metallographic analysis. Annex 2 of ASTM International Standard ASTM B811 recommends measuring the fraction of the long hydrides oriented radially in the cladding wall. This measurement is generally reported as $F_{(N)}$. However, for various reasons, other quantitative metallographic metrics are also used. These metrics include a radial hydride continuity factor (RHCF) and the radial hydride concentration. Each metric basically evaluates the extent to which the hydrides provide a “brittle” pathway across the cladding wall and empirical correlations among the various metrics, Figure 15, are available. The empirical correlations among the various metrics suggest that the metrics are similar and that choices among the metrics are basically personal preference. Commercial image analysis packages are also available to quantify hydrogen content, hydride orientation and hydride lengths in “properly prepared” metallographic specimens (Colas).

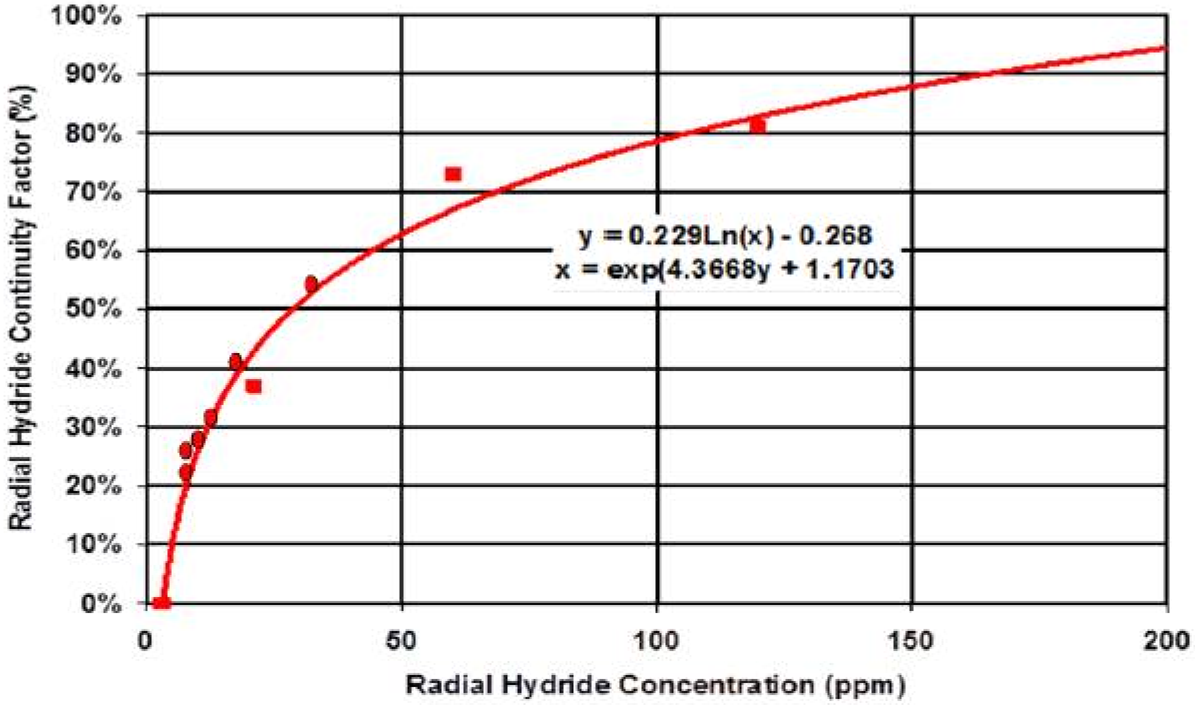


Figure 15: Empirical Correlation of Radial Hydride Continuity Factor with Radial Hydride Concentration (Presentation 10, Slide 9)

Characterization of the mechanical properties of as fabricated fuel tubes from a variety of vendors is underway (Lavender) to provide a data base for use in predictive models. One goal of these tests is to ultimately provide statistically valid separate effects measurements of the effects of hydrogen, irradiation, alloying and fabrication on clad behavior. Unfortunately, these characterizations are relatively new and the irradiated materials data base remains under development. Currently a significant fraction of the mechanical test data for irradiated material uses ring sections of cladding cut from the used fuel. The fuel pellets are removed from the test sections and the ring is compressed between two anvils, Figure 16. The ring compression test (RCT) is used to minimize the cost of preparing irradiated materials for testing and to maximize the amount of data that can be collected from a section of irradiated fuel. However, to enable direct comparisons between irradiated and non-irradiated materials, non-irradiated samples are being tested using the RCT (Ruiz Hervias, Korinko). Ring samples of irradiated and non-irradiated materials are also being tested in tension and used in hydride reorientation studies.

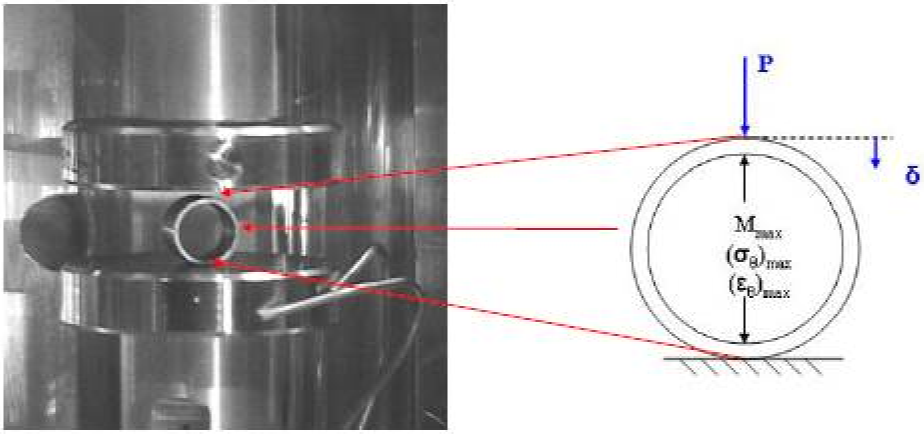


Figure 16: Experimental Setup for a Ring Compression Test (Presentation 16, Slide 7)

Data from the ring compression tests at various temperatures are analyzed to estimate the effects of hydrogen and hydride morphologies on the response of used fuel cladding to thermo-mechanical conditions anticipated during drying, storage, transport and disposal. Analysis techniques include reporting the deflection or offset strain to fracture (Billone) and the area under the load deflection curve or displacement energy density at fracture (Mozzani). These data show that strain to fracture is dependent on test temperature and on the hydride morphology which may be modified by hydride reorientation tests. For example, as-irradiated ring sections of M5 cladding from high burnup fuel tubes that contained less than 100 ppm hydrogen were ductile at test temperatures down to 298K. Hydride reorientation tests at 673K and 90 MPa hoop stress did not alter the mechanical response but when the reorientation stress was increased to either 110 or 140 MPa, a ductile-to-brittle transition was observed at temperatures below approximately 335K, Figure 17. It is important to recognize that the term, ductile-to-brittle transition was used at the workshop to describe a marked decrease in the fracture resistance of the material because of a change in one or more of the test variables. Test variables influencing the transition in most of the tests include: hydride content and orientation, temperature and cladding alloy. The transitions described simply represent the results from testing a specific set of samples and should not be confused with standardized DBTT transitions determined (primarily for bcc alloys) by impact or fracture mechanics type testing.

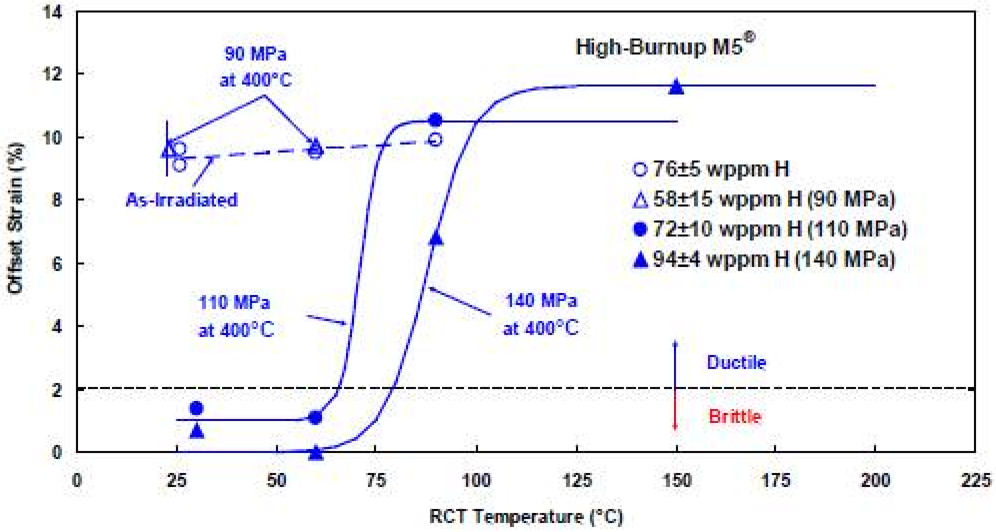


Figure 17: Ductile-to-Brittle Transitions in Irradiated M5 Cladding Samples after a Hydride Reoriented Treatment. Note the absence of such a transition in the as-irradiated material and after a low stress reorientation treatment. (Presentation16, Slide 9)

Tests of ZIRLO cladding from high burnup fuel tubes also showed ductile-to-brittle transitions that were introduced by hydride reorientation treatments, but the effects of temperature and hydride reorientation test conditions differed from that seen for the M5 cladding. Tests on ring sections of the irradiated ZIRLO cladding suggested that the ductile-to-brittle transition temperature could exceed 393K, depending on the hydride reorientation conditions.

Tests using non-irradiated ZIRLO cladding sections also showed radial-hydride-induced ductile-to-brittle transitions and found that the apparent transition temperature depended on the hydrogen content, the hydride reorientation stress and the test technique (Korinko). Hydrogen charged test sections having 100 to 800 ppm hydrogen were tested in the as-charged condition and after hydride reorientation treatments at 90, 130 and 170 MPa. Ductile-to-brittle transitions did not occur unless the reorientation stress was 130 or 170 MPa and the observed transitions were sensitive to the hydrogen content and were generally higher for samples with lower hydrogen contents, Figure 18.

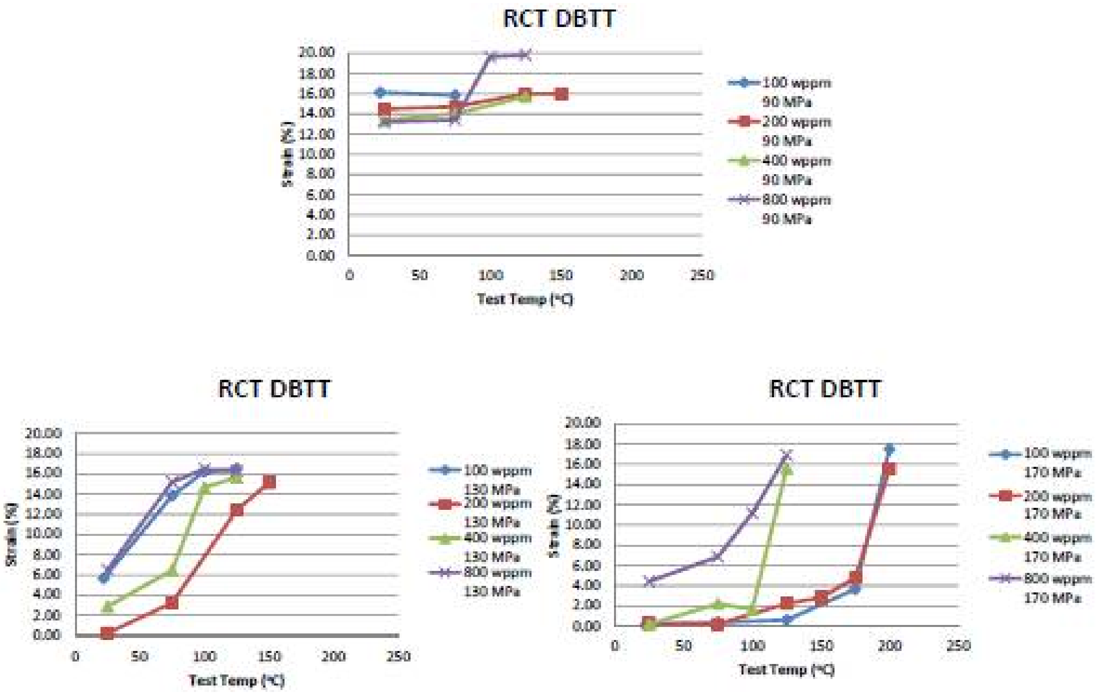


Figure 18: Ductile-to-Brittle Transitions in Non-Irradiated ZIRLO Cladding after Hydride Reorientation Treatments (Presentation 17, Slide 23)

Furthermore, the DBTT's measured by three point bend tests (3-PBTs) of tube sections did not duplicate the ring test results made for sections from the same tubes (Korinko). In the three point bend test the ductility related more to the total hydrogen than to the amount of hydride reorientation. The three point bend data provide a very different characterization of the transition than the RCT tests. This result was anticipated because 3-PBTs induce axial bending stresses while RCTs induce hoop bending stresses (primarily). Other results show that measured transition temperatures in hydrided zirconium alloys is sensitive to the test strain rate and was increased by 100K when the test strain rate was increased from 10^{-5} to 10^{-2} (Louthan).These observations point to the need to evaluate the relevance of test results to postulated accidents and to consider the potential for axial bending under accident conditions.

Room temperature ring compression tests were also conducted on samples from non-irradiated CWSR Zircaloy-4 tube sections that were hydrogen charged and creep-tested at various stress and temperature conditions for times up to 700 hours (Eapen). Similar tube sections were given 2 hour hydride reorientation treatments at 673K. The effect of the hydride reorientation stress on the displacement energy density at fracture was similar for the samples regardless of the time spent at elevated temperatures, Figure 19, although, the creep tested samples (long time at elevated temperatures) were slightly more susceptible to hydride reorientation.

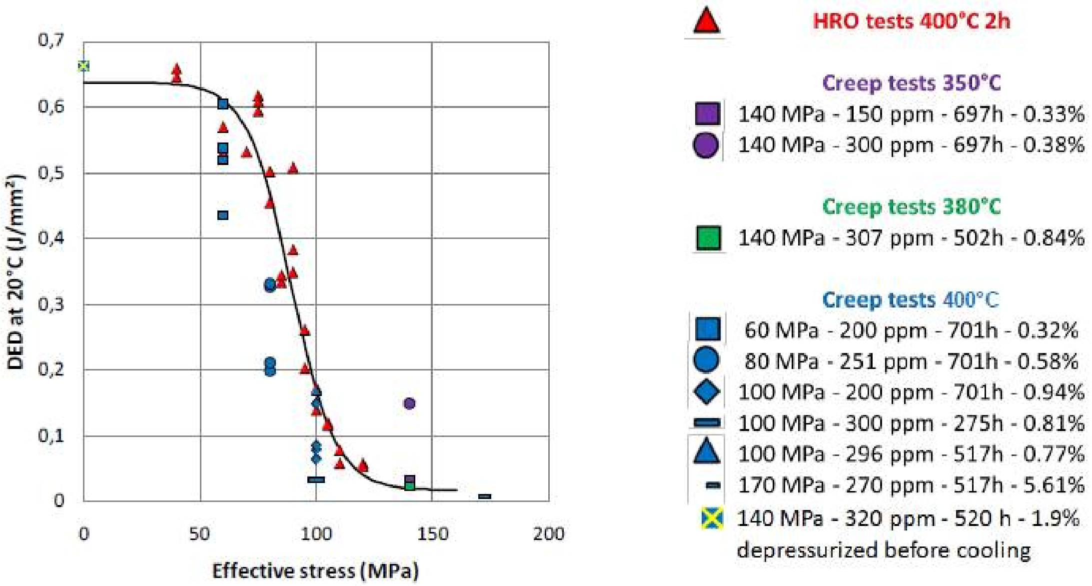


Figure 19: Comparison of Ring Compression Test Data for Hydrided, Non-irradiated CWSR Zr-4 Samples Tested after Long Term Creep Tests and Short Term Hydride Reorientation Treatments. Results show that the hold time at elevated temperatures may have impacted the reorientation process. (Presentation 15, Slide 13)

Tests with the non-irradiated tube sections demonstrated that specimens with different hydrogen contents and tested under the same conditions could end up with different ductilities as measured by the DED. As the 623K creep test data in Figure 19 demonstrate, the specimen having the lowest hydrogen content had the lowest ductility probably because all the hydrides dissolved during the elevated temperature hold and reorientation readily occurred while the non-dissolved hydrides in the specimen having the higher hydrogen content may have inhibited the reorientation process. These differences are apparent in Figure 20 and, in the sense that increasing the hydrogen content increased the post RHT ductility, are consistent with the data shown in Figure 18.

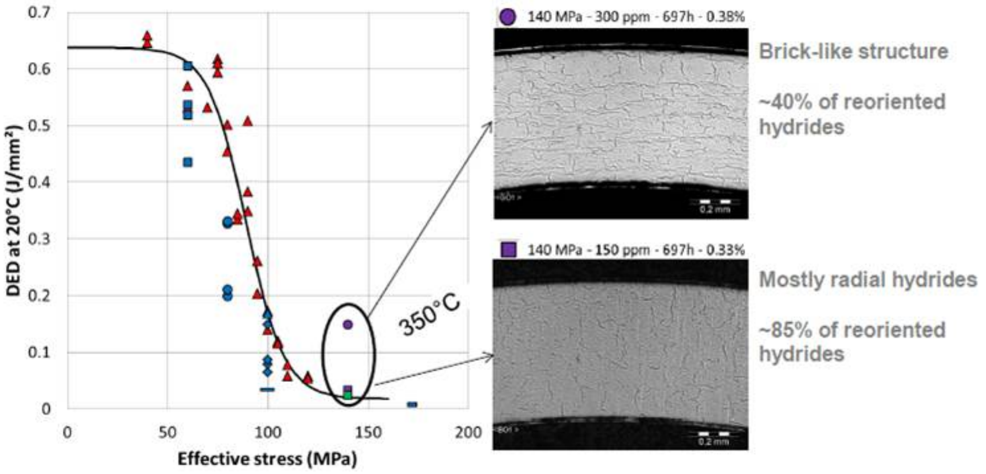


Figure 20: Test Data Demonstrating the Importance of Hydrogen Content on Hydride Reorientation and on Subsequent Mechanical Behavior (Presentation 15, Slide 14)

Three key points emerged from the workshop:

1) The performance of zirconium alloy claddings is sensitive to alloy chemistry, hydrogen content and thermo-mechanical history thus data developed for alloy A may not be applicable to alloy B.
2) Irradiation alters the behavior of cladding alloys thus data and analyses developed on non-irradiated materials should be carefully evaluated before being applied to used nuclear fuel claddings, and
3) The mechanical response of cladding alloys is very sensitive to test technique and the onset of brittle fracture under any given set of test conditions does not necessarily predict brittle behavior in actual service.

These points are totally compatible with the literature and, coupled with other observations, demonstrate the need for international standards to bring consistency to the assessments used to predict the long term performance of used nuclear fuel cladding under extended dry storage conditions.

3. Workshop Conclusions

An overall conclusion developed from the presentations and discussions (formal and informal) at the workshop is that the fundamental processes that could lead to hydrogen-induced degradation of irradiated zirconium-based alloys during long term storage are well understood, in a general sense. However, the susceptibility of zirconium alloys to hydrogen induced degradation is sensitive to:

a) Alloy chemistry and manufacturing process,
b) Irradiation history,
c) Hydrogen content,
d) Manufacturing and operational induced non-uniformities
e) Hydride morphology, including distribution and orientation, and
f) Post irradiation thermo-mechanical exposures.

Understanding the effects of these material variables on the degradation sensitivities has been enhanced by coupling detailed optical metallographic observations with non-standard mechanical property measurements and fundamental hydrogen-in-zirconium alloy data. Relevant information is wide spread throughout the open literature. Unfortunately, the usefulness of many, open literature, oral presentations, written reports, even peer reviewed journal articles, has often been minimized because details of material preparation and testing are not shared. For example, a report may present the total hydrogen content in an alloy but make no mention of the hydride morphology. Additionally, even though it is reasonably well recognized that behaviors determined for any given alloy, irradiated in any given reactor, are not necessarily transferable to other situations, there is a tendency to try to establish, a “one-size-fits-all” data base and to use such bases to support regulatory guidelines. Emergent recommendations and guidelines must provide a technical basis that includes the variations in materials response and demonstrates that the variations are understood in terms of material and system variables.

Laboratory practices used in the evaluation of the behavior of hydrided zirconium alloys should, to the extent possible, be standardized or at least consistent, across the nuclear industry. Such standardization would increase the ease of information transfer among organizations and enhance the value of the transferred information. Additionally, there should be an increased effort to fully integrate the relevant data and analyses emerging throughout the global nuclear community. For example, this workshop had no AECL representative and very little work supporting heavy water reactors was described; therefore, data directly relevant to commercial heavy water reactors is lacking in this white paper.

Workshop presentations included data developed by testing irradiated and non-irradiated materials with considerable emphasis on developing, in non-irradiated materials, hydride morphologies representative of irradiated fuel cladding. Clearly, the data developed from non-irradiated materials provides information which aides in understanding the behavior of irradiated materials. However, it is also clear that the behavior of non-irradiated materials is not directly applicable to the behavior of used fuel cladding. This is illustrated in the determinations of the threshold stress for hydride reorientation. Data developed for non-irradiated alloys under uniaxial tension suggest that the critical stress varies from about 60 MPA to above 100 MPa while analysis of irradiated materials behavior shows hydride reorientation at stresses as low as 28 MPa. Differences in the response of irradiated and non-irradiated materials to thermo-mechanical treatments suggest that, even if the hydride morphology is matched, care must be taken in using non-irradiated material behavior to predict the performance of used nuclear fuel cladding and fuel assembly alloys. Additionally, a better understanding of alloy-to-alloy variations in the susceptibility to stress orientation and the impact of stress state on stress orientation must be developed.

4. Workshop Recommendations with Emphasis on Developing International Standards

The data and analyses presented at the workshop demonstrate the need for ASTM International to facilitate information exchange in the nuclear industry by standardizing laboratory practices related to the effects of hydrogen and hydrides on the behavior of fuel assemblies during long term storage. These practices include processes and techniques to:

a) Determine the local and bulk hydrogen content in a sample,
b) Characterize the hydride morphology by optical microscopy,
c) Determine the hydride orientation,
d) Evaluate hydride reorientation and memory effects,
e) Measure the effects of hydrogen on mechanical behavior,
f) Determine ductile-to-brittle transformation temperatures that are applicable to evaluate fuel assembly behavior for storage and transfer processes, and
g) Relate observations made on non-irradiated materials to the behaviors of used nuclear fuel cladding and components.

Recommendations related to each of these areas are discussed in the following sections of this summary.

4.1 Determining the Hydrogen Content

The zirconium-hydrogen phase diagram (Bulletin of Alloy Phase Diagrams, Vol. 11, p. 386, 1990) shows that the minimum hydrogen content of δ-hydride in equilibrium with the α-Zr matrix increases from approximately 14,300 ppm at 823K to about 17,000 ppm at 298K. The temperature of a hydride rim on a fuel element in a PWR will depend on the oxide film thickness and the temperature of the primary coolant at that location. Both film thickness and coolant temperature vary with the location of the fuel element in the fuel assembly and with the location of the assembly in the reactor as well as with position along the length of the fuel rod. In any event, the maximum hydrogen concentration in the hydride rim is approximately 17,000 ppm unless irradiation changes the phase equilibrium. Measurements at room temperature of the hydrogen in δ-hydrides in non-irradiated Zircaloy-4 are consistent with the phase diagram and show that 17,000 ppm hydrogen in local regions that have 100% volume fraction hydrides (Colas). The phase diagram also shows that at temperatures below about 373K the hydrogen solubility in zirconium is essentially zero. Therefore, at room temperature, hydrogen-containing zirconium alloys have at least two equilibrium phases, the hydride with 17,000 ppm hydrogen and the α-matrix with essentially 0 ppm hydrogen. The average hydrogen content in the material determines the volume fraction of the hydrides in the microstructure. This average or bulk hydrogen content can be measured by inert gas fusion or hot vacuum extraction techniques (ASTM E 146-83). Commercial instruments capable of measuring bulk hydrogen contents (from the ppm level to thousands of ppm) in zirconium alloys are readily available and may be used to determine the hydrogen content of a bulk specimen.

The bulk hydrogen content in a specimen can be correlated to the hydride's volume fraction. This volume fraction may then be empirically related to the measured bulk hydrogen content and/or correlated with the fraction calculated through analysis of the phase diagram. Relationships between the determinations of hydride volume fraction and bulk hydrogen content may be established. The empirical relationship developed from image analysis will be similar, if not identical, to one calculated using the phase diagram. However, because metallographic preparation generally enlarges the apparent volume of the hydrides, image analysis determinations are recommended. Image analysis software may be used on properly prepared metallographic samples to determine the radial variation in hydrogen content across the wall of a used fuel cladding (Colas). A key element in the use of metallographic samples to quantify the local hydrogen (hydride) content in a used fuel element is assuring “proper, reproducible metallographic preparation.” To obtain such assurances examples of properly prepared, under etched and over etched samples should be made available throughout the nuclear industry, and standardization, to the extent possible, of metallographic preparation techniques across the nuclear industry is recommended.

4.2 Characterizing Hydride Morphology by Optical Metallography

The goal of metallographic preparation is to obtain a surface that, on examination in a light microscope, provides reproducible images of the grain and/or twin structure, any surface films on material edges (for example the oxide film on the outer surface of irradiated cladding), the size shape and distribution of second phase precipitates, flow lines and/or other microstructural features of interest to the metallographer. Specimen preparation to determine the microstructure of used nuclear fuels often focusses on preserving the edges on a specimen cross section and etching to bring out the image of any precipitated hydride. Metallographic images from samples that successfully accomplished these two purposes are shown throughout this summary. However, due to site-to-site difference in metallographic preparation procedures, there are variations among the images even when the hydride content is similar as previously shown in Figure 1.

Modern technology has mechanized the grinding and polishing processes so that scratch free surfaces may be readily obtained. Additionally, the automatic polishing equipment provides a flat smooth surface with a very thin damage layer that may be removed during etching. Etchants are selected and etching times are controlled so that the long hydride phases appear as dark lines in bright field microscopy around 100X magnification. The lines are hydride stacks with the individual short hydride segments within the stack not generally resolved by optical microscopy. Occasionally the orientation of a stack may be such that the hydride appears as an angular rather than a linear precipitate. Because the etchant corrodes the hydride-metal interface faster than either the hydride or the matrix, over etching tends to increase the apparent width of the hydride and therefore increases the apparent volume fraction of hydride in the microstructure. Universal use of standardized etching procedures (etchant, application technique and time) would reduce the site-to-site variations among images and thereby enhance information exchange. However, the etching characteristics differ among the various cladding alloys and it may be necessary to recommend standardized, alloy-specific etching procedures.

Metallographic examination of a properly etched specimen allows determination of many aspects of the hydride morphology, including: the total amount of hydride present, the radial distribution of hydrides across the cladding wall, the thickness of the oxide film on the outer cladding surface, the hydrogen content and hydride distribution in the zirconium layer on barrier cladding, the presence (or absence) of hydride rims and/or blisters and the width of any hydride depleted layer in the microstructure. Standardization or at least the development of a standard guide for metallographic preparation techniques is recommended as a companion to the standardization of measurement techniques for determining the local hydrogen distribution in an alloy and/or for describing the hydride orientation in used fuel cladding.

4.3 Determining Hydride Orientation

Early work (Marshall and Louthan, Trans. ASM, 1963) correlated hydrogen-induced ductility losses in non-irradiated Zircaloy-4 tubing with hydride orientation. This work showed that for the specific samples tested, the room temperature tensile ductility was essentially zero if 50 ppm hydrides (or more) were oriented perpendicular to the tensile axis. Subsequent work confirmed the importance of hydride orientation and demonstrated variability in material response to oriented hydrides. For example, M5 with about 58 wppm had long radial hydrides and was ductile at room temperature in a ring compression test (Billone). Long hydrides tend to precipitate so that the normal to the long hydride is parallel to the axis of a tensile stress applied to the material during hydride precipitation. A critical or threshold stress is required to produce stress-induced reorientation and the value of this critical stress was a function of specimen orientation, texture, fabrication history and composition. Nuclear fuel cladding is now manufactured so that hydrides are oriented circumferentially in the as-irradiated cladding wall. However, post irradiation thermo-mechanical exposures may cause reorientation of the hydrides and adversely impact the mechanical behavior of the cladding. The potential for hydride-induced degradation in nuclear fuel cladding is frequently estimated by determining relationships associated with the orientation of precipitated hydrides. The microstructure of heavily stress oriented specimens, Figures 5c, 6b and 10 for example, contains long hydrides that:

1) Are obviously strongly oriented so that the hydride normal is parallel to the stress axis,
2) Have preferentially precipitated in association with another hydride, and
3) Provide long, relatively straight pathways for cracking through hydride stacks.

Zirconium alloys containing these and similar hydride microstructures are expected to be brittle at low temperatures under tensile and pinch loading conditions.

The macroscopic association of brittle cracks with stress oriented hydrides, Figure 13, coupled with extensive semi-quantitative relationships among measured ductility and observed hydride morphology provide the technical basis for developing relationships between material response and a measure of the hydride orientation. Measures of hydride orientation include the determination of the fraction of hydride oriented radially in the cladding wall, the ppm of oriented radially hydride, the continuity of a radial pathway across the cladding, the average length or radial hydrides and other metrics measurable by image analysis techniques. As shown in Figure 15, empirical relationships can be established between some of those metrics. It is recommended that the procedures for determining the various metrics be summarized in a standard guide and that relationships among the various metrics be established. At this point there is no clear cut reason for preferring any specific metric although it may be beneficial to recommend a single metric to facilitate comparisons in the hydride reorientation and memory effects areas of study.

4.4 Hydride Reorientation and Memory Effects

Hydride precipitation in as-irradiated used fuel claddings is generally circumferential for at least two reasons: 1) the fuel cladding manufacturing process produces a combination of materials characteristics that favor the nucleation of circumferential hydrides, and 2) the cooling water pressure on fuel elements in the reactor minimizes or eliminates the hoop tensile stresses acting on the cladding. Therefore, while the fuel is in the reactor, circumferential hydride nucleation dominates the precipitation process. Hydrogen is introduced into the tube wall by corrosion of the external surface. Therefore, hydrogen initially accumulates near the outer surface of tube. The thermal gradient across the cladding combines with the hydrogen accumulation process to maximize the hydrogen content at the outer surface, just beneath the corrosion produced oxide film. Hydride rims often develop in high burnup fuel claddings because of the corrosion associated with the long reactor exposures. Typical microstructures of high burn up fuel claddings (Figure 5) illustrate the heterogeneous distribution and circumferential orientation of the hydrides in as-irradiated cladding. If the fuel were to remain in the storage pool and the cooling water were to maintain the cladding temperature below about 373K the hydride morphology would not change during storage. Even though hydrogen atoms in solid solution in zirconium alloys are very mobile at 373K, the nearly zero hydrogen solubility at this temperature prevents hydrogen permeation through the zirconium lattice and the subsequent coarsening or alteration of the hydride microstructure. However, when the fuel is removed from the water pool and transferred to dry storage, the cladding may reach temperatures as high as 673K due to the release of decay heat and the lack of water or gas to facilitate heat transfer from the fuel.

Heating to 673K increases the hydrogen solubility in the cladding from essentially zero to approximately 200 ppm; because of the high diffusivity of hydrogen at this temperature, hydride dissolution rapidly occurs until the equilibrium hydrogen concentration (200 ppm) is reached in the zirconium alloy matrix or until all the hydride is dissolved. The 673K temperature also anneals the dislocation loops or nests associated with the hydrides precipitates. Fuels can be separated into two categories, based on the hydrogen content and fuel drying temperatures:

1) Claddings with hydrogen concentrations less than the hydrogen solubility limit at the peak cladding temperature reached during drying. All the hydrides are dissolved. For example, all the hydrogen will be dissolved in claddings with less than 200 ppm if the drying temperature reached is 673K, and
2) Fuel claddings with hydrogen concentrations above the hydrogen solubility at the maximum temperature reached by the cladding during drying. In this case, some hydrides will remain precipitated and will generally be circumferentially oriented.

Cooling of the dried fuels from 673 to 373K will cause precipitation of the dissolved hydrogen but the conditions for reprecipitation differ from those experienced when the fuel cooled in the reactor system. The rod internal pressure places a hoop tensile stress on the cladding wall and this stress could be sufficient to cause stress-induced reorientation of the hydrides. If all the hydrogen was in solid solution and the rod internal pressure were high enough the reorientation process would favor radial hydride precipitation. If there are non-dissolved hydrides in the cladding, these pre-existing hydrides will influence subsequent hydride precipitation may inhibit the stress induced reorientation.

The conditions necessary for hydride reorientation vary with several cladding and fuel parameters. As discussed above, claddings with lower hydrogen contents (less than 200 ppm for example) may experience significantly more hydride reorientation than nearly identical claddings with higher hydrogen contents. Additionally, the hoop stress (due to rod internal pressure) necessary to produce stress orientation varies among the commercial cladding alloys and, for any given alloy, is sensitive to stress state, cooling rate and other cladding variables. The technical data base necessary to predict hydride reorientation after drying is not generally available in the open literature. Furthermore, the information presented at this workshop suggests that analytical models that use data developed from uniaxial tests of non-irradiated materials are not adequate to predict degradation processes in used fuel assemblies. Efforts to minimize the extent of this data gap should be a major focus for future programs. These programs should be conducted in concert with test development activities designed to determine the effects of hydrides and hydride reorientation on the mechanical properties of used fuel cladding.

4.5 Measuring the Effects of Hydrides on Mechanical Behavior

The need for post-irradiation examination of spent fuel cladding, an expensive and time consuming process, could be significantly reduced if fundamental and/or empirical correlations between measurements on irradiated and non-irradiated materials were established and understood. Two programmatic areas to assist in this effort were discussed at the workshop: 1) the production of typical irradiation hydride morphologies in non-irradiated cladding alloys, and 2) mechanical behavior characterization using ring sections machined from fuel cladding.

The hydride morphology in irradiated fuel cladding is, as previously discussed, very heterogeneous and varies significantly with reactor and fuel cladding types, Figure 5. A high burnup barrier cladding fuel from a BWR may develop a hydride-rich zone in the inner liner, while a hydride rim may lie below the outer surface oxide film on the cladding from as-irradiated high burnup PWR fuels. Laboratory techniques to develop hydride rim on the outer (Simskey, Ruiz Hervias) and inner (Korinko) cladding surfaces have been developed. Ring compression, ring tension and bend tests with rim-containing non-irradiated samples may, in principle, duplicate, the results from irradiated cladding sections.

The underlying purpose of the mechanical tests on irradiated or non-irradiated materials is to develop data that can be reliably used to assess the performance of fuel rods and assemblies during the handling, transportation and transfer operations that will follow long term dry storage of spent nuclear fuel. This capability will be based on the output from analytical models that typically require material properties such as yield and ultimate strength, tensile ductility, fracture toughness (fracture mechanics and/or impact) and other standard property measurements. Input from modelers will be needed to assure that the necessary behaviors are determined. The effort to correlate material behavior in a ring compression or ring tension test with mechanical properties measured by more or less standard mechanical tests is recommended to be a four-step process.

1) Develop an ASTM International Standard or Standard Guide for the ring compression test.
2) Develop and conduct, with non-irradiated cladding samples, a test program to correlate measured mechanical responses during the ring compression or ring tension test with mechanical property data that will serve as inputs to analytical modeling programs.
3) Establish that the correlations developed on non-irradiated cladding alloys can be applied to irradiated claddings.
4) Define the range of applicability for applying the correlations to cladding alloys having the anticipated variations in hydride contents and morphologies.

It is also recommended that the four step effort be a multiple laboratory study and, if practical, include international cooperation. Additionally, as part of step one, an effort should be made to assess the potential value of including bend testing in the standard. Three- and four-point bend tests should be evaluated. The four-point bend tests may be of significant value because of the larger section size exposed to the highest stress during testing.

4.6 Determining Ductile-to-Brittle Transition Temperatures

A ductile-to-brittle fracture transition is a marked change in the fracture resistance of a material induced by changes in one or more system variable. The ductile-to-brittle transition temperature is the temperature below which the fracture resistance of the material is very low. Unfortunately, the transition temperature depends on several material and system variables. Strain rate, hydrogen content, specimen design, hydride orientation and morphology, alloy chemistry and oxide film thickness influence the transition temperature of zirconium based alloys. The data presented at the workshop described a ductile-to-brittle transition temperature for selected alloys and showed that this temperature was only applicable to one cladding alloy that had a specific hydrogen content and hydride morphology, and was evaluated by a specific test conducted at a relatively low strain rate. After completion of emergent efforts to standardize the ring compression and ring tension test (or other tests such as the bend test) and relate the RCT data to results from qualified tests using more common mechanical property measurements, it may be possible to defines DBTTs for irradiated cladding alloys under conditions that would be relevant to the handling, transportation and disposal of used nuclear fuels.

4.7 Relating Non-Irradiated and Irradiated Materials Behavior

Cost and material availability provide major drivers to qualify processes and procedures that provide data relevant to irradiated materials by testing non-irradiated samples. However, very limited data has been collected where the irradiated and non-irradiated material samples were prepared from the same cladding stock, had the same hydride microstructures and were tested by the same techniques. There are alloy-to-alloy and heat-to-heat differences in the performances of non-irradiated materials tested by identical techniques and similar differences are found in irradiated materials. Additionally, irradiation impacts basic behaviors such as hydrogen solubility, alloy microstructure, strength, ductility and the susceptibility to stress orientation. Progress is being made in duplicating the hydride microstructures typical of irradiated cladding alloys in non-irradiated samples, but other aspects of irradiation-induced changes in material behavior have not been duplicated. Significant benefits would be gained if test results from non-irradiated materials could be directly related to irradiated materials behavior. Unfortunately, qualified data bases demonstrating such relationships are marginal, at best. Therefore, it is recommended that materials data derived from the testing of non-irradiated materials be carefully evaluated by multiple investigators before being used to predict the behavior of used nuclear fuels. While expensive, future testing plans should include irradiated samples with pellets in-place to verify and/or compliment the non-irradiated testing.

5. Conclusion

The large variations in material response to thermo-mechanical exposures make the development of, and adherence to, standards to characterize and measure hydrides and their impacts on the long term performance of used nuclear fuels highly desirable. Such adherence could provide more consistency across the nuclear industry and will maximize the value of most observations. Additionally, programs are recommended for developing the technical data base necessary to

1) Relate the behavior of non-irradiated materials to the behavior of irradiated materials by investigating both behaviors using samples from the same cladding alloy (data for non-irradiated material have minimal value unless companion data for irradiated material are available), and
2) Relate material behavior during a ring compression, tensile and bend tests to mechanical property data developed under qualified ASTM International standard testing.
3) Quantify hydride orientation in cladding and test samples.