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P.S. Korinko, R. L. Sindelar, R. L. Kesterson, T. M. Adams[1]

[1]Savannah River National Laboratory, Aiken, SC 29808, USA

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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. Samples were charged with 200 and 800 wppm gaseous hydrogen and subjected to a radial hydride growth treatment at three stresses. These samples were characterized and tested using a simple ring compression test. Ductile to brittle transition temperatures were determined for these samples.

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. Samples were hydrogen charged in 99.95% purity H_2 and subjected to a radial hydride growth treatment (RHGT) by pressurizing to the required internal pressure at room temperature and heating to 400°C to achieve hoop stresses of 90, 130, and 170 MPa, and cooling at 5°C/hr to 200°C for details see Refs. 2 and 3.

The as charged and aged hydrogen content was determined using inert gas fusion. Sections that were 8 mm long were characterized. Metallographic sample preparation and examination were aslo conducted using standard grinding and polishing techniques. The etchant used to reveal the radial hydrides consisted of nitric and hydrofluoric acid and hydrogen peroxide.

Ductile to brittle transition tests were conducted on samples that were charged with 200 and 800 wppm hydrogen using a ring compression test (RCT). The samples were wire electrical discharge machined from the 38 mm long tubes. These samples were then subjected to a RCT using the method described in [1 and 2]. The samples were tested on an Instron 4507 load frame with MTS renew software. Displacement was measured using a $\pm$ 4 mm deflectometer and force was measured using a 100 N load cell. While the RCT is a non-standard test but is very useful for comparing different treatments and hydrogen contents. The RCT was conducted at constant crosshead speeds of 5 mm/s with a programmed displacement of 1.7 mm. Data were captured at a rate of 500 Hz. Samples were tested at room temperature and elevated temperature in 50°C increments. A test was run at temperature 25°C cooler than the highest temperature if no cracking was observed during the test.

Results and Discussion

Figure 1 shows the axial hydrogen profile for samples in the as charged condition and after RHGT. Note that there is a significant variation along the length of the tube. The axial temperature profile of the charging furnace follows a similar characteristic and it is expected that these results are due to the axial thermal gradients. The central portion of the charged tube has a fairly uniform concentration and this section of the tubing was used for the RCT samples.

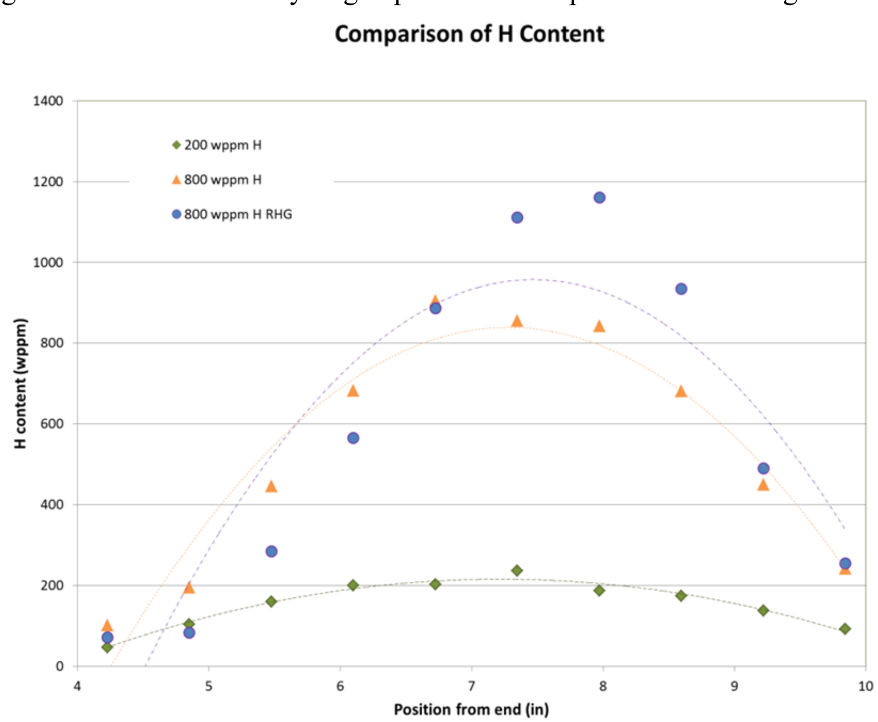

Fig. 1. Hydrogen concentration for as hydrided and RHGT ZIRLO tubing.

The microstructures of the samples were characterized using optical microscopy. The as charged samples exhibited uniform hydride precipitation; the generally expected structure of ZIRLO clad is one that exhibits a “rim” type structure [4]. However, since the RHGT promotes mobility of a fraction of the hydrogen in the material, it was expected that the uniform hydride morphology would be acceptable. The fraction of mobile hydrogen that is available for reorientation depends on the total content. This consideration indicates that lower hydrogen content will exhibit a higher fraction of radial hydrides. Further, if the radial hydrides promote embrittlement, then clad with hydrogen contents greater than the solubility limit, may be embrittled more than higher hydrogen content materials. Figure 2 shows the results of a simple model based on hydrogen solubility equations for dissolution and precipitation. For instance, a sample containing 200 wppm hydrogen heated and cooled in a controlled manner between 400 and 200°C should exhibit 100% new hydride. If this hydride is formed at a suitable stress level, then it could be radial oriented and promote embrittlement that is observed in RCT. Likewise, if a sample initially containing 800 ppm of hydrogen is exposed to the same treatment, about 200 wppm will be in the new hydride precipitates and consequently about 25% of the structure would be in the radial orientation if the stresses during the thermal treatment are sufficiently high to promote radial hydride growth.

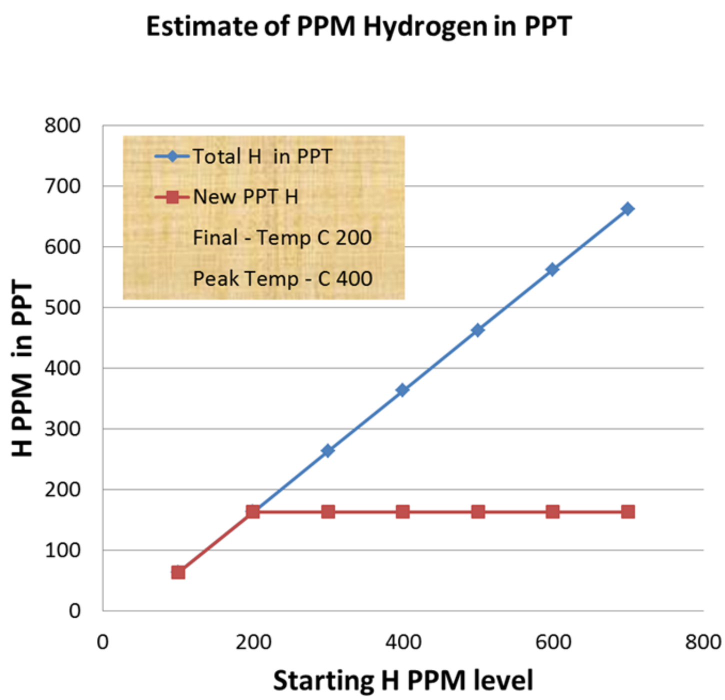

Fig. 2. Results from a simple model to predict the extent of “new” hydride precipitation [4].

Figures 3 and 4 show the microstructure of samples containing 200 and 800 wppm hydrogen after the thermal exposure modeled in Fig. 2. ZIRLO samples in the as-charged condition exhibit a uniform hydrogen precipitation, as shown in Fig. 4a for a sample chph1larged with 800 wppm H. As can be seen from these micrographs, the morphology of the new hydrides is dependent on the applied hoop stress as well as the initial hydrogen content. The hydrogen charging method produces some internal hydride core at 800 wppm. The hydrides are initially oriented circumferentially. The morphology is modified when exposed to the RHGT treatment. The samples exposed to the RHGT with an internal stress of 90 MPa initially, exhibit a few radial hydrides. The fraction of radial hydrides increase in the samples treated at 130 and 170 MPa. The sample with 200 wppm at 170 MPa consists of an almost checkerboard pattern. Several researchers have derived hydride orientation factors [1]; however, these were not measured for these samples. The relative amount of radial hydrides compared to circumferential hydrides for the samples charged to 800 wppm H is appears lower. This result is consistent with the simplified hydride precipitation model, where in a sample with 200 wppm cycled from 400 to 200°C will have the potential to have 170 wppm of the 200 wppm H formed in new hydrides, i.e., radially precipitated; whereas, the sample with 800 wppm, will also have 170 wppm H in the new hydrides, or only about one fourth of the hy-

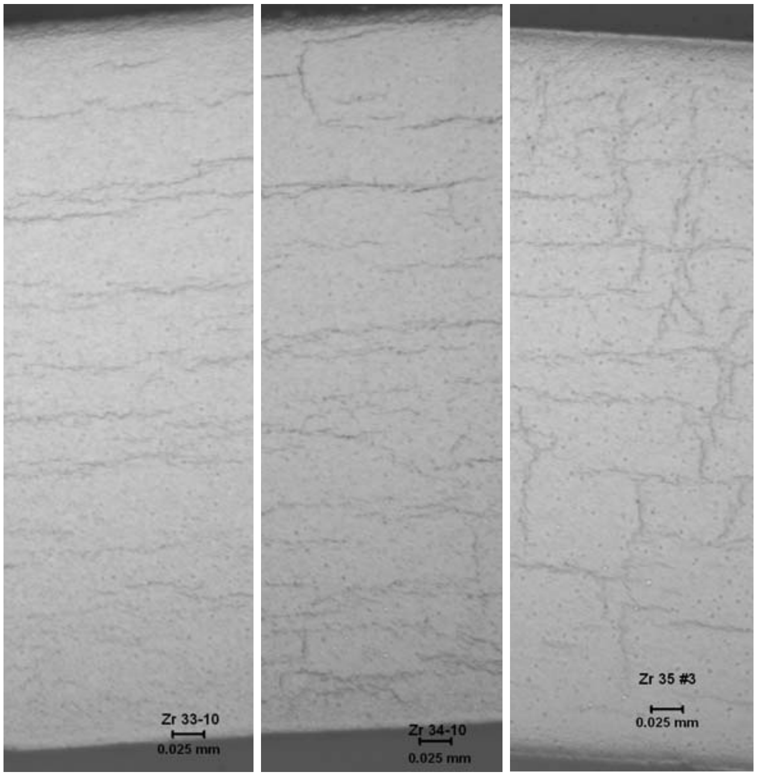

Fig. 3. ZIRLO sample charged with 200 wppm H (a) as hydrided (b) RHGT 90 MPa, (c) RHGT 130 MPa and (d) RHGT 170 MPa

drides will be radially oriented.

Ring compression tests were conducted on samples at room temperature and higher. A typical series load displacement curves for the 200 wppm sample subjected to the 170 MPa RHGT is shown in Fig. 5. As can be seen, samples were tested from room temperature to a temperature at which there was not a brittle fracture during RCT. Since the samples were tested to a fixed displacement, several cracks may have initiated and during the test. The presence of the cracks is indicated by load drop. The cracks generally, initiated at either the 3:00 or 9:00 followed by cracks at the 6:00 or 12:00 positions.

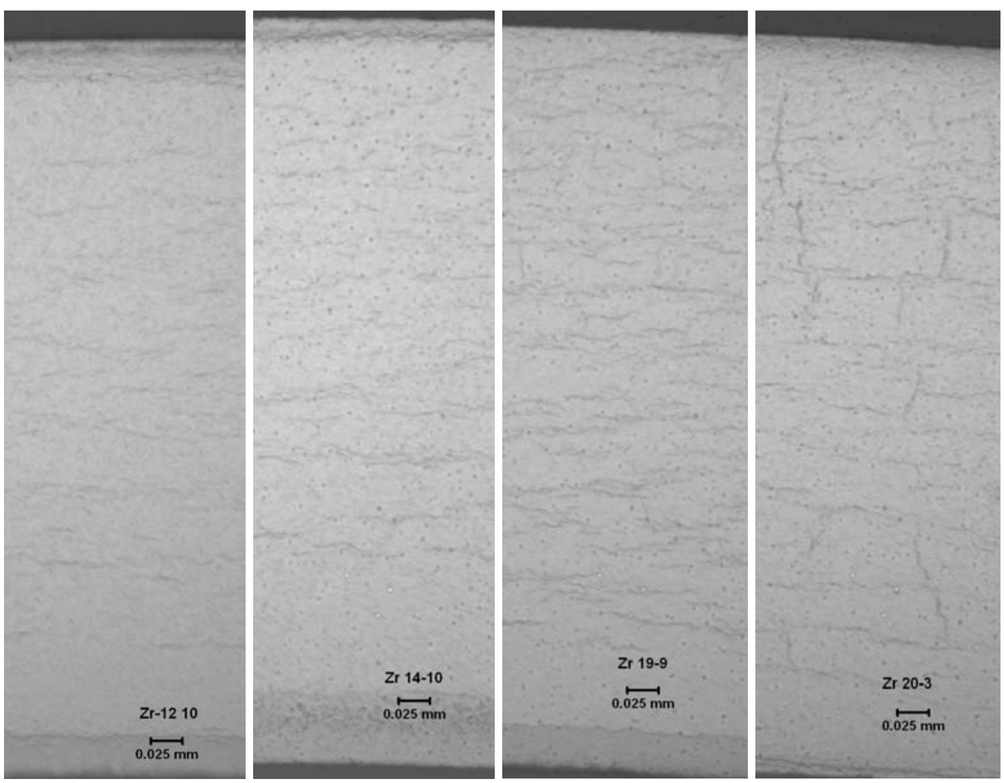

Fig. 4. ZIRLO sample charged with 800 wppm H (a) as hydrided (b) RHGT 90 MPa, (c) RHGT 130 MPa and (d) RHGT 170 MPa

A structural ductile to brittle transition temperature was developed using a calculated strain parameter based on the plastic displacement to the first load drop / crack and the original diameter, $\varepsilon_{eff}=\delta/D_o$. When this "strain" was greater than 5%, the samples were considered ductile while values less than this were considered brittle. DBTT curves for the 200 wppm samples are shown in Fig. 6. The data shown indicate that the 90 MPa stress was inadequate to promote embrittlement, while there was a transition for samples subjected to the RHGT with stresses of 130 and 170 MPa. The effective DBTT strains are listed in Table 1.

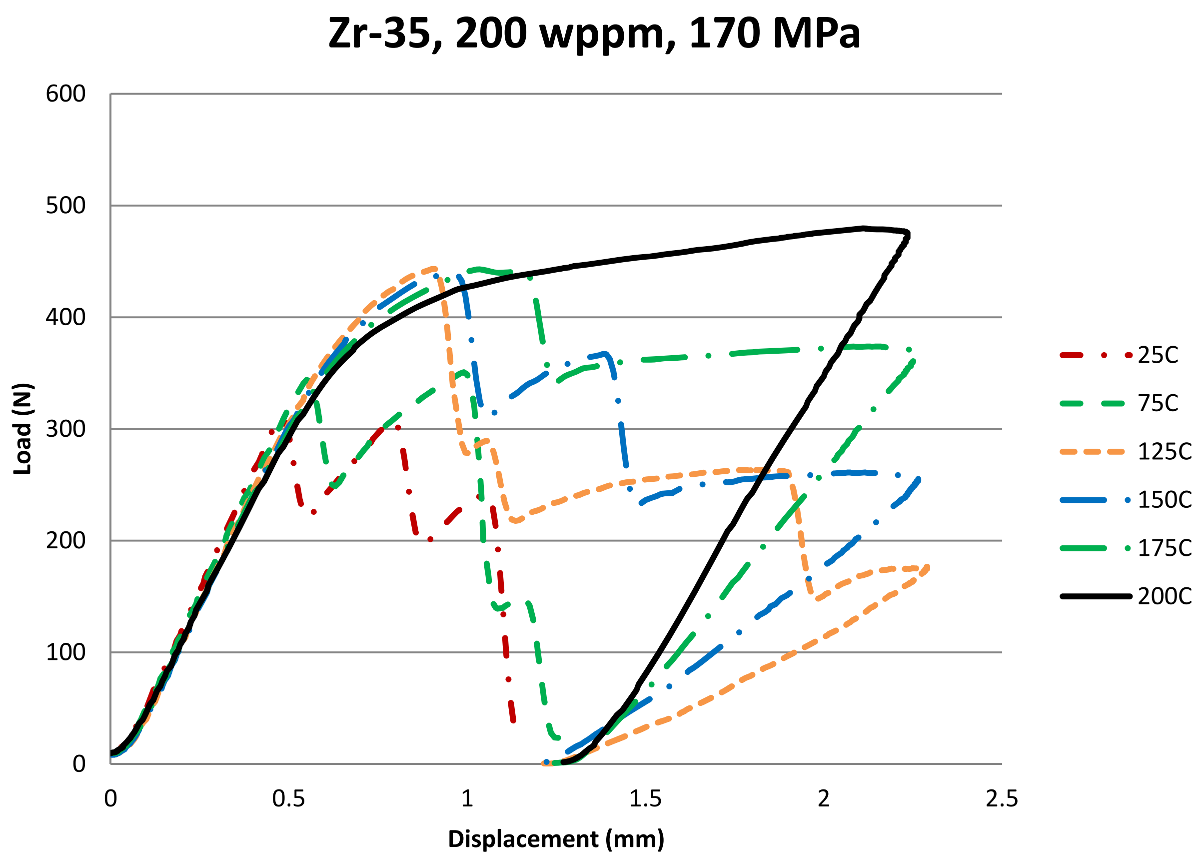

Fig. 5. Load Displacement data for samples charged with 200 wppm H and RHGT at 170 MPa.

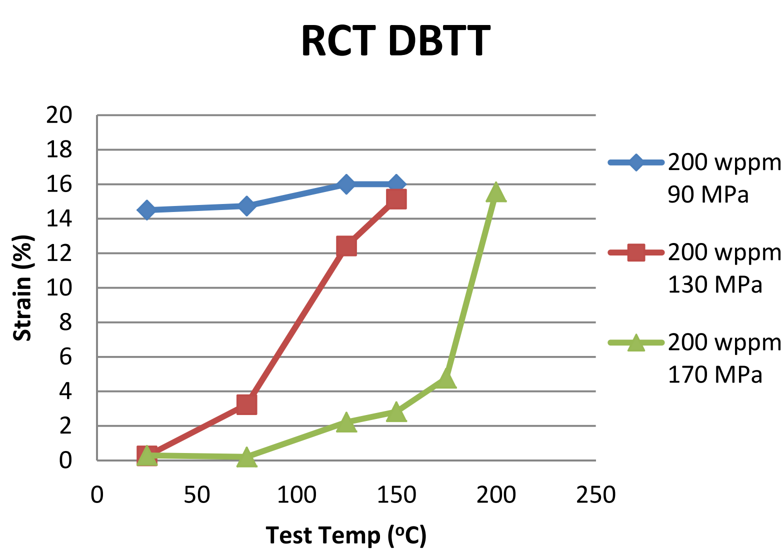

Fig. 6. Ductile to brittle transition temperature test results for ZIRLO charged with 200 wppm H and subjected to RHGT at stresses indicated.

Table 1. DBTT strain data for samples charged with 200 and 800 wppm H and subjected to RHGT at 90, 130, and 170 MPa.

		Temperature (^{o}C)						
wppm	Stress (MPa)	25	75	100	125	150	175	200
200	90	14.50	14.74		16.00	16.00		
200	130	**0.26**	**3.23**		12.43	15.14		
200	170	**0.29**	**0.20**		**2.22**	**2.82**	**4.76**	15.56
800	90	13.19	13.41	19.65		19.83		
800	130	6.52	15.19	16.48		16.27		
800	170	**4.42**	6.87	11.18		16.92		

Summary and Conclusions

ZIRLO samples charged with 200 and 800 wppm H were subjected to RHGT with internal stresses of 90, 130, and 170 MPa were tested to determine the ductile to brittle transition temperature using radial hydride compression testing. The radial hydride growth treatment developed the radial structure at internal stresses of 130 and 170 MPa. Only a few radial hydrides were formed at 90 MPa. The fraction of radial hydrides was greater for the 200 wppm samples. The DBTT varied from 25°C to 175°C depending on the hydrogen content and the stress treatment.

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