Effect of reduced hydride connectivity on the mechanical strength of Zr-Nb-Sn alloy via grain growth

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1. Introduction

Recently, various studies on hydride embrittlement and mechanical property degradation of Zirconium alloys have been conducted. Some of these studies claim that hydride embrittlement can be mitigated with larger grain sizes [1–3]. Larger grain size can improve the hydride embrittlement resistance by reducing the hydride network interconnectivity in Zircaloy has been theoretically shown by Qin et al.[1]. Electron backscatter diffraction (EBSD) characterizations by Kim et al.[3] experimentally showed that hydride interconnectivity decreases with larger grain sizes subjected to annealing. Based on these findings suggesting a hidden advantage of grain growth, this study verifies the effect of reduced hydride connectivity with annealed grains on mechanical strength.

Annealing heat treatments, such as RXA (recrystallized annealing), PRXA (partial recrystallized annealing), and SRA (stress-relief annealing), reduce the residual stress in the material that occurs during the cladding manufacturing process and recover it to a more uniform microstructure. While these heat treatments are performed to maintain optimal in-reactor conditions, this study focuses on the annealing effect of elevated temperatures in the vacuum drying process on the material's microstructure during dry storage. The potentially beneficial effect of grain size increase on the mechanical integrity of zircaloy cladding may represent a new factor in the evaluation of acceptable recrystallization and grain size increase during dry storage.

2. Theoretical backgrounds

A significant ductility drop, known as the ductile-to-brittle (DBT) transition, was found by Bai et al. [2] to occur in situations where cracks can propagate along hydrides when sufficient numbers of hydrides are present. Qin et al.[1] have shown that a theoretical model (Eq.1) that explains a larger grain size can hinder the interlinked hydride network formation in Zircaloy.

$$C_H^{B,C} = C_H^S\, exp\left(\frac{\Delta G_{Strain} + \Delta G_{inc.}}{1.66RT}\right)\left[p + q\, exp(-\frac{\kappa}{RT})\right] \quad (1)$$

Where $C_H^{B,C}$ is the critical hydrogen content of the bulk alloys for the interlinked hydride network formation, C_H^S is the terminal solid solubility, ΔG_{Strain} is the hydride formation strain energy per mole, and $\Delta G_{inc.}$ is the interaction energy between the hydride and applied stress. R is the gas constant, T is the absolute temperature, κ is the hydrogen segregation potency at the grain boundaries, and p and q ($p + q = 1$) represent the probability of the intra- and inter-granular hydride that forms near the pre-existing hydride tip, respectively [1][3][4].

κ in Eq. (1) causes hydrogen to precipitate preferentially at grain boundaries, making interconnected hydrides more easily formed. A higher q value lowers $C_H^{B,C}$, causing the DTB to occur at a lower hydrogen content. A smaller grain size within the same volume of material increases the density of grain boundaries and can increase the q value of Eq. (1) [1]. Conversely, a larger grain size can lower the q value, causing DTB to occur at higher hydrogen concentrations. This indicates that larger grain sizes have higher resistance to hydride embrittlement. Fig. 1 [3] shows the relationship between grain size and a fully interlinked hydride network formation.

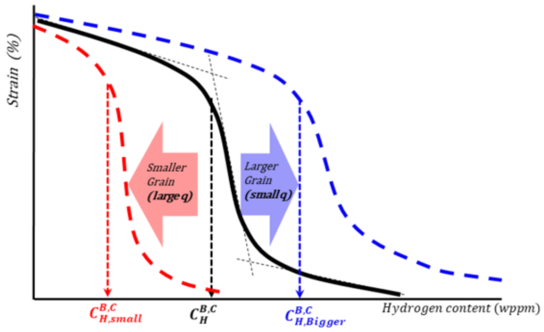

Fig. 1. Relationship between grain size and a fully interlinked hydride network formation which is related to DTB transition [3]

3. Experimental setups

To investigate the effect of annealing on hydride connectivity and resulting mechanical integrity, the stress-relief-annealed (SRA) Zr-Nb-Sn alloy with an outer diameter of 9.5 mm and a wall thickness of 0.57 mm was used in the experiments. The material is reactor-grade as-received cladding tube. The chemical composition of the material is presented in Table I. The as-received Zr-Nb-Sn alloy specimens were cut to 8 mm lengths for the mechanical tests.

Table I: Chemical composition of Zr-Nb-Sn alloy (mass%)

Element	Zr	Nb	Sn	Fe	O
Zr-Nb-Sn alloy	Bal.	0.924	0.944	0.094	0.124

Some samples were charged with hydrogen before the annealing experiments. Hydrogen charging of the specimens was performed at 400 °C. The hydrogen determinator (OH-p) was used to measure the hydrogen content before and after annealing. Then, the samples were annealed at various temperatures and durations. The samples were isothermally annealed at 450, 475, and 500 °C for various periods such as 4, and 12 h. For the annealing, the oxidation of the samples was prevented by maintain a vacuum condition of 1.0×10^{-5} torr in the test section (quartz tube) (see Fig. 2). The applied heating rate was 3–5 °C/min until the specimen reaches the target temperature, and the applied cooling rate was 0.5–1 °C/min. The temperature of the specimen was measured using a K-type thermocouple attached to the surface of the specimen.

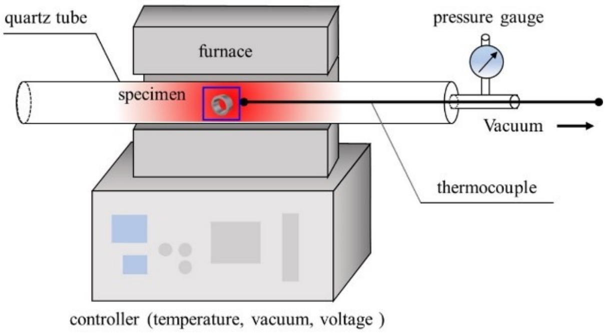

Fig. 2. Schematic of the quartz tube for annealing.

After that, EBSD analysis was performed for the observation of hydride morphologies and microstructural characterization. The accelerating voltage, and step size were set to 20 kV, and 0.06 μm, respectively. For post-mechanical testing, an INSTRON-8516 testing machine was used for ring compression tests (RCTs). The machine is equipped with the uniaxial load cell(100 kN, accuracy: ±0.05% of indicated load), and the displacement rate was 0.033 mm/s.

4. Results

4.1 Reduced hydride connectivity with grain growth

The relationship between the grain size and a fully connected hydride network formation revealed the possibility of intentionally increasing the grain size of Zircaloy prior to dry storage. Hence, the hydride morphologies are examined for different post-annealing Zircaloy matrix microstructures. Hydrogen-charged Zircaloy samples are annealed at 450, 475, and 500 °C for 12 hours, respectively. The average grain size after annealing measured by EBSD analysis is shown in Table II. As the annealing temperature increased, the grain size also got bigger.

Table II: Averaged grain size of the 12 h annealed samples

	(1) As-received	(2) 450 °C	(3) 475 °C	(4) 500 °C
Grain size (μm)	0.89 (±0.07)	0.91 (±0.07)	1.18 (±0.13)	2.97 (±0.16)

In Fig. 3, as grain growth progresses with increasing annealing temperature, the hydride connectivity decreases owing to the reduced grain boundaries which serve as preferred sites for hydride precipitation. As can be noted in the hydride morphology of the as-received specimen (Fig. 3(a)), hydrides are precipitated in the form of aligned lines. Then, grain growth removes preferred sites for the hydride precipitation, and decreases hydride connectivity thereby increasing hydride embrittlement resistance. In Fig.3 (c) and (d), notable disconnections of hydride interlink are seen in bigger grain sizes resulting from increased annealing temperatures.

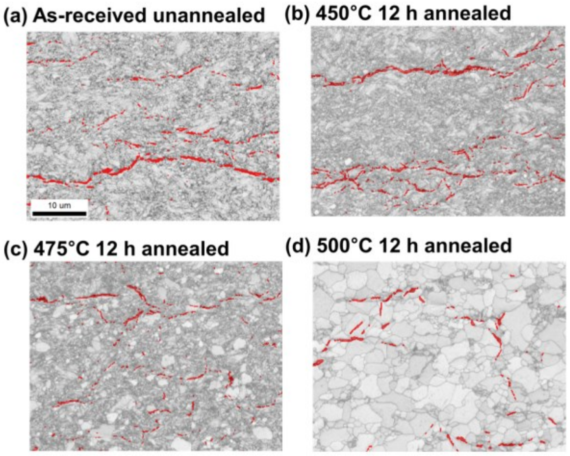

Fig. 3. EBSD analysis on the hydride connectivity after annealing: (a) As-received unannealed sample (594 ppm), (b) 12 h annealed at 450 °C (600 ppm), (c) 12 h annealed at 475 °C (610 ppm), (d) 12 h annealed at 500 °C (595 ppm).

4.2 Mechanical test results

The effect of annealing on the mechanical integrity of the cladding is further investigated for hydrogen-charged specimens using a ring compression test (RCT). The hydrogen-charged samples were annealed at 475 °C for 0, 4, and 12 h, and RCT was performed. The hydrogen concentrations of the three samples subjected to RCT were all in the range of 600 ± 10 ppm after annealing. The mechanical test results are shown in the Fig. 4 and Table III.

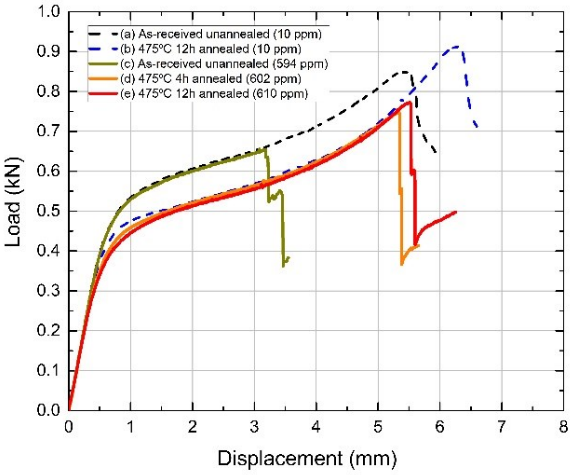

Fig. 4. Load-displacement curve of (a) As-received, (b) 475°C 12 h annealed, (c) 475°C unannealed with hydrogen concentration 594 ppm, (d) 475°C 4 h annealed with 602 ppm, (e) 475°C 12 h annealed with 610 ppm.

Table III. Strain energy density (SED) of the mechanical tests

Specimen	SED [kJ/m]
(a) As-received unannealed (10 ppm)	0.417
(b) 475°C 12h annealed (10 ppm)	0.463
(c) As-received unannealed (594 ppm)	0.203
(d) 475°C 4 h annealed (602 ppm)	0.352
(e) 475°C 12h annealed (610 ppm)	0.366

The Strain energy density (SED) represents the maximum strain energy density that a specimen can retain until failure occurs. The strain energy was calculated over the area from the load-displacement curve until the first major load drop occurred. Then, the strain energy was divided by the length of the specimen (8 mm) to obtain the SED in kJ/m.

Annealing of the hydrogen-free as-received specimen at 475 °C for 12 hours led to the increase of SED by 11% (0.417 to 0.463 kJ/m) under RCT (curves (a) and (b) of Fig. 4 and Table III). The SED increase is primarily due to the grain growth of the material which induces the increase of ductility. The grain size increased by 20% (+0.177) from 0.89 μm to 1.067 μm by annealing at 475 °C for 4 h, and increased by 33% (+0.296) to 1.186 μm by annealing at 475 °C for 12 h. For the hydrogen-charged specimen (curves (c),(d), and (e) of Fig. 4 and Table III)., SED increased significantly by 80% (+0.163) from 0.203 to 0.366 kJ/m.

While the ductility increase of the matrix is present for the hydrogen-charged specimen, the extra increase in the cladding ductility is considered related to the hydride microstructures. The presented ductility increase with the reduced hydride connectivity is a hidden benefit of grain growth for high burnup cladding.

5. Conclusions

As grain growth progresses with increasing annealing temperature, the intergranular hydride connectivity decreases owing to the reduced grain boundaries which serve as preferred sites for hydride precipitation. The reduced hydride connectivity significantly increases cladding ductility. The improved hydride embrittlement resistance with a larger grain size may motivate to intentionally heat-treat the spent fuel cladding such that it has desirably grown-grains prior to dry storage if it outweighs the adverse effect of increased creep rate.

However, it needs to be carefully practiced because the larger grain size generally deteriorates the mechanical strength of the material and can have a substantial effect on the creep behavior.

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