Hydride-Induced Embrittlement of Zirconium Alloy Claddings during Long-Term Dry Storage of Spent Nuclear Fuels

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1. Introduction

Spent nuclear fuels (SNFs) are expected to be stored in dry storage systems for extended periods until a final decision for disposal is made. The US NRC [1] mandates that SNFs be safely and readily retrievable from storage systems for further processing or disposal. Additionally, it requires that the SNF cladding be protected against gross rupture unless the SNFs are confined. For Canada Deuterium Uranium (CANDU) SNFs, it is crucial that the cladding temperature remains below 180°C to ensure the long-term integrity of the fuel cladding during dry storage [2]. However, there is still uncertainty regarding whether the SNF cladding undergoes microstructural changes during prolonged storage, potentially leading to aging-related embrittlement, even at temperatures below 180°C.

When the SNF cladding cools below 200°C during long-term dry storage, it undergoes a ductile-brittle transition (DBT), becoming brittle. This phenomenon commonly occurs in zirconium alloys that contain hydrogen [3]. It has been observed [4] hydrides, which fracture during impact testing at low temperatures below the DBT, do not fracture at high temperatures above the DBT. However, the exact causes of the DBT phenomenon and the brittle fracture of hydrides at temperatures below the DBT remain unknown.

However, under high strain-rate conditions, such as those in impact tests, or under triaxial stress states during fracture toughness tests with compact tension specimens, all types of hydrides precipitated in zirconium alloys tend to fracture, regardless of their orientation. This tendency is especially pronounced at low temperatures below the DBTT [4]. In contrast, at high temperatures above the DBTT, even radial hydrides tend to become ductile and do not fracture. Thus, the DBT appears to be related to the occurrence of hydride fracturing, as indicated in Refs. 4. Specifically, if a low strain rate is applied, resulting in less fracturing of hydrides in the SNF cladding, then the DBTT of the SNF cladding determined at this low strain rate is of little significance. The aim of this work is to provide experimental evidence that the DBT is caused by hydride fracturing and to identify the underlying causes of the DBT in zirconium alloys with hydrogen.

2. Experimental procedures

Fracture toughness tests were conducted using 17 mm curved compact tension (CCT) specimens, which were cut from a quad-melted Zr-2.5Nb pressure tube. Hydrogen was introduced into the CCT specimens up to 200 ppm either electrolytically or through gaseous charging. The hydrogen-charged specimens then underwent homogenization treatments at various temperatures, followed by furnace cooling. Their actual hydrogen contents were determined using a LECO RH 404 analyzer. Fracture toughness tests were conducted on the CCT specimens at temperatures ranging from RT to 300°C, in accordance with ASTM E1820-01 using a single specimen method. A pre-fatigue crack of around 1.7 mm was introduced into all the CCT specimens with an R ratio (P_{min}/P_{max}) of 0.1 to yield an initial relative crack length, or a_o/W of 0.5. During testing, the CCT specimens were loaded at a constant displacement rate of 0.1 mm/min, as monitored by two linear variable differential transducers (LVDTs). The crack advancement was monitored using the direct current potential drop (DCPD) method, and each test was terminated after less than 4 mm of crack growth. J-R curves were obtained according to ASTM E1152.

3. Results and discussion

Figure 1 shows the fracture toughness, dJ/da (in MPa), of Zr-2.5Nb specimens containing hydrogen ranging from 0 to 200 ppm, as a function of temperature. Their fracture toughness decreased with increasing hydrogen content. The hydrogen-charged Zr-2.5Nb specimens exhibited a DBT in the temperature range of 100 to 150°C, which was not observed in the as-received (AR) specimen containing 5 ppm H.

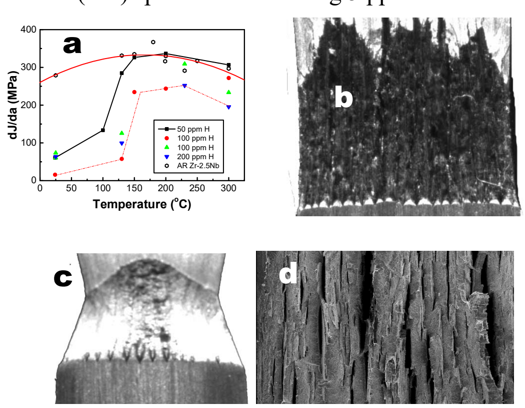

Fig. 1. (a) Fracture toughness, dJ/da (in MPa) of Zr-2.5Nb tube specimens containing 50 to 200 ppm H with temperature, (b) fracture patterns of Zr-2.5Nb with 100 ppm H during fracture toughness tests at (b) RT, (b) 300°C and (d) SEM image of the fractured surface obtained at RT shown in (b).

The results shown in Fig. 1 reveal that the DBT of hydrided zirconium alloys is related to the ordering of hydrogen dissolved in the zirconium lattice, leading to the δ-to-γ hydride transformation in zirconium alloys. In fact, the δ-to-γ hydride transformation is similar to an ordering transformation, corresponding to decreases in entropy. Conversely, the γ-to-δ hydride transformation is similar to a disordering transformation, representing increases in entropy

According to Kim's entropy-stress law [5], entropy decreases generate compressive stresses in hydrided zirconium alloys, leading to embrittlement and fracturing of hydrides (Fig. 1), while entropy increases produce tensile stresses, leading to softening and no hydride fracturing (Fig. 1). Compelling evidence for entropy decreases resulting from the δ-to-γ hydride transformation is provided by the observations of heat release from hydrided zirconium alloys upon cooling. Thus, no hydride fracturing at 300°C, as shown in Fig. 1c, is attributed to tensile stresses generated by entropy increases, due to the γ-to-δ hydride transformation and hydride dissolution, upon heating. In contrast, hydride fracturing at low temperatures, as shown in Figs. 1 and 1b, is caused by compressive stresses generated by entropy decreases, due to the δ-to-γ hydride transformation and hydride precipitation. As a result, the DBT of hydrided zirconium alloys is driven by entropy changes caused by the γ-to-δ hydride transformation or its reverse, and by simultaneous hydride dissolution and precipitation during heat and cooling, respectively.

Accordingly, the significance of these entropy-driven internal compressive stresses generated in the SNF cladding lies in their potential to increase hardness and embrittlement, which could severely impact the retrievability of SNFs by making the cladding more prone to fractur during handling, transportation, and repackaging. This increased brittleness raises the risk of cladding failure, potentially leading to fuel fragmentation and release of radioactive material, thereby complicating the safe retrieval and transfer of SNFs, posing a concern to violate the NRC requirement. Root observed that the rate of the δ-to-γ hydride transformation in a Zr-2.5Nb alloy increased noticeably as the temperature decreased below 100°C, but became sluggish at temperatures above 100°C. During long-term storage, CANDU SNFs cool below 100°C relatively quickly compared to LWR SNFs, as the initial cladding temperature for the dry storage of CANDU SNFs is typically below 180°C [2]. As a result, CANDU SNFs become more brittle over time due to prolonged exposure to low temperatures after the onset of dry storage. Additionally, if the entropy-driven compressive stresses in the SNF cladding are high, delayed hydride cracking (DHC) can occur, leading to the growth of axial cracks, a phenomenon observed in an irradiated Zr-2.5Nb tube stored in a pool [6]. In contrast, it takes over 30 years for LWR SNFs to cool to temperatures as low as 100°C [7], meaning that the embrittlement process occurs much later than in CANDU SNFs.

In this study, fracture toughness tests were performed at a low strain rate (0.1 mm/min) to assess crack propagation resistance, rather than to evaluate the impact-induced DBTT. While high-strain-rate tests, such as impact testing, are necessary for evaluating embrittlement risks under dynamic loading conditions (e.g., handling and transport), low-strain-rate tests remain valid for evaluating toughness and delayed hydride cracking (DHC) susceptibility. The concern regarding Billone's test conditions [8] was not solely due to the low strain rate, but rather to the interpretation of DBTT results under conditions where minimal hydride fracturing was observed. This distinction is crucial when applying test data to assess the long-term performance of SNF cladding under different service conditions.

4. Conclusions

The fracture toughness of hydrided Zr-2.5Nb decreases with hydrogen content, showing the pronounced DBT ranging between 100 and 150°C. At RT, hydrides readily fracture in high-hydrogen specimens, leading to brittle fracture, while, at 300°C, no hydrides fracture, resulting in ductile fracture. The continued δ-to-γ hydride transformation and hydride precipitation during cooling increase entropy-driven compressive stresses generated in the SNF cladding, making it more brittle. SNF cladding discharged after high burnup becomes more susceptible to gross rupture as it cools below 100°C, likely due to the enhanced δ-to-γ transformation, high hydrogen content, and irradiation hardening. Higher strain rate mechanical testing should be prioritized to better understand the DBT and fracture toughness under conditions simulating handling and storage risks.

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