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Effects of hydrogen contents on the mechanical properties of Zircaloy-4 sheets

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ABSTRACT

The purpose of this study was to investigate the effects of hydrogen contents on the mechanical properties of Zircaloy-4 sheets. Zircaloy-4 specimens were gaseously hydrided up to 832 ppm H and then tested at 25, 100, 200, 300 and 400 °C. Tensile specimens were chosen to understand the ductile-to-brittle transition associated with hydrogen content. Scanning electron microscopy was used to examine the fracture surface. The results showed that, at 25 °C, a ductile-brittle transition occurred on the Zircaloy-4 specimen with hydrogen contents between 538 and 832 ppm H. The behavior was not observed as the temperatures were above 100 °C. In the temperature range of 100–300 °C, the specimens charged with 712 ppm H and below exhibited good ductility. The early occurrence of the strain localization for the specimens with hydrogen content larger than 456 ppm H was found at temperatures higher than 200 °C. Fractographic examinations indicated that quasi-cleavages features were observed as the hydrogen content was 712 ppm H and above at the temperatures below 100 °C, whereas ductile fracture occurred for all the hydrided specimens tested at temperatures higher than 200 °C. Stress-strain curves suggested that yield points were observed on the unhydrided specimens while the phenomenon was suppressed on the hydrided ones.

1. Introduction

In light water reactors, zirconium alloys are widely used as nuclear fuel cladding and in-core structural components, owing to their unique combination of low neutron absorption cross-section, good corrosion resistance and superior mechanical properties. Gaseous hydrogen is generated during service through the reaction: $Zr+2H_2O \rightarrow ZrO_2+2H_2$ and radiolytic decomposition of water. As a result, one of the major issues is the up-take of hydrogen and the subsequent precipitation of hydrides due to a low solubility of hydrogen in zirconium alloys. It is known that the precipitated hydride may severely degrade ductility and fracture toughness of the materials [1]. In addition, the nuclear industry is pushing to extend the fuel burnup to higher levels to have higher economic efficiency. The impact of the extension may lead to an increase in hydrogen pickup and internal pressure of fuel cladding. This may exacerbate the hydrogen embrittlement of Zircaloy cladding, and therefore, it is a concern during reactor service or dry storage of spent nuclear fuel [2]. In addition, during extended dry storage, hydride reorientation from hoop to radial direction may provide an additional embrittlement mechanism as the cladding temperature decreases below the ductile-to-brittle transition temperature. As a result, hydrogen embrittlement of fuel cladding stands out as being of high importance for potential degradation and needs to be addressed for cladding integrity [3]. Interim Staff Guidance-11, Revision 3 (ISG-11) used by the US NRC staff requires [4] that for all fuel burnups, the maximum cladding temperature should not exceed 400 °C during normal conditions of storage. The temperature will limit the reorientation of hydrides into radial hydrides that would make fuel cladding brittle, when fuel cooled down after vacuum drying.

Extensive efforts have been made to study the effects of hydrogen contents on the mechanical properties of hydrided zirconium alloys [1,5–12]. These studies have indicated that a ductile-to-brittle transition exists. It was found [7] that the hydrided Zircaloy-4 exhibits a ductile-to-brittle transition at room temperature in the hydrogen content range are between 400 and 800 ppm. Bai and his co-workers [8,9] performed a series of tensile tests for hydrided Zircaloy-4 specimens at 20 and 350 °C. Their results showed that the reduction of area for Zircaloy-4 is drastically reduced at room temperature above a certain level of hydrogen content, while the transition disappears at 350 °C. Furthermore, the embrittlement effect depends on prior thermomechanical treatment and sheet thickness [8,9]. Similar results also suggested [10–12] that the transition disappears at temperatures higher than 100 °C, and that Zircaloy-4 exhibited negligible ductility at room

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temperature. The hydrogen embrittlement of Zircaloy cladding is not only related to the hydrogen concentration, but also related to the morphology and orientation of zirconium hydrides [13]. Those findings reported in the previous literature indicated that the sensitivity of hydrogen embrittlement of Zircaloy-4 is affected by multiple factors, including material prior treatment, microstructure and testing conditions. In addition, it is noted that previous research works [8–10] used the abrupt change of the value of reduction of area as a definition to represent the "ductile-to-brittle transition" for the tensile-tested specimens. We follow the definition in this work.

Although the ductile-to-brittle transition of Zircaloy-4 was observed, the literature mentioned above did not provide systematic understanding concerning the ductility change as a function of temperatures and hydrogen contents simultaneously. It is not clear whether the ductile-to-brittle transition region would change for those Zircaloy-4 charged with higher hydrogen contents at different temperatures or, if it does, what level of change it might exhibit. The objective of this study was intended to systematically investigate the effects of hydrogen contents up to the 900 ppm level on the mechanical properties of Zircaloy-4 at temperatures ranging from room temperature to 400 °C. This approach was to simulate the mechanical behavior of Zircaloy-4 subjected to the high burnup condition. An attempt was made to develop a map to characterize the ductile to brittle transition behavior and ductility changes of Zircaloy-4 as a function of temperatures and hydrogen contents. The experimental results could be used as a reference to scientific understanding and regulatory needs.

2. Experiments

The commercial Zircaloy-4 (Zry-4) material was used in this study. The material had a composition of Sn 1.47, Fe 0.21, and Cr 0.10 wt% and impurity (in parts per million) of 1480O, 5N, 6H and 138C, Zr the balance. Sheet specimens with dimensions 105 mm × 25 mm × 1.6 mm were used in the as-received condition. Zry-4 sheet specimens were uniformly hydrogen-charged by a thermal cycling process to the targeted hydrogen content levels of 300, 450, 600, 750 and 900 ppm, respectively. The hydrogen charging temperature was initially set at 200 °C with an increment of 10 °C for each thermal cycle until it reached the maximum temperature 300 °C. The detailed hydriding process was described elsewhere [14]. Hydrogen concentrations were determined by the inert-gas fusion method using a HORIBA (EMGA-930) hydrogen analyzer. The reported values of hydrogen concentration were the average of at least three measurements. Table 1 summarizes the values of targeted and measured hydrogen contents.

To understand the mechanical behavior of the Zry-4 charged with 5 hydrogen contents, miniature tensile tests were performed. Fig. 1 shows the geometry of the specimen. The tests were carried out at five temperatures: 25, 100, 200, 300 and 400 °C. For the tests at T > 25 °C, a thermocouple was attached to the specimen in the gauge length region. The desired temperature was controlled to ±1 °C. Both unhydrided and hydrided specimens were tested to fracture on a MTS 810 Servo Hydraulic Testing System at an engineering strain rate of 5×10^{-3}/s. The stress-strain curve was used to determine 0.2% offset yield strength (YS) and ultimate tensile strength (UTS). The reduction of area (RA) was calculated from the dimensional changes between the original and ruptured tensile samples.

Table 1
The targeted hydrogen content levels and the measured hydrogen contents of Zircaloy-4 sheets.

Targeted hydrogen content (ppm)	300	450	600	750	900
Measured hydrogen content (ppm)	359	456	538	712	832

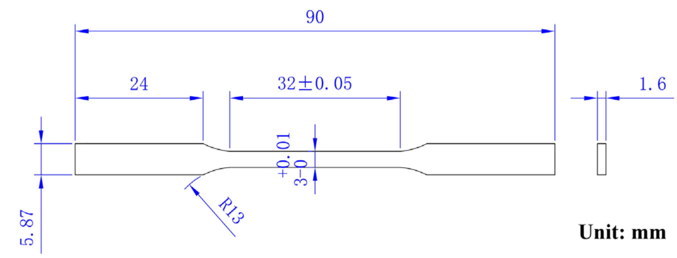

Fig. 1. The geometry of the tensile-tested specimen.

3. Results and discussion

3.1. Mechanical tests

Fig. 2 shows the correlation between UTS and hydrogen concentration. The value of UTS slightly increased as hydrogen concentration increased. A similar trend was observed with the YS (Fig. 3). As expected, both UTS and YS decreased with increasing temperature. Fig. 4 depicts the RA at different temperatures with respect to hydrogen concentration. On the curve for 25 °C, Zry-4 exhibits a gradual decrease in the RA from 69% to 56% as the hydrogen content increases from 0 to 538 ppm H. Between 538 and 832 ppm H at 25 °C there is a distinct ductile-to-brittle transition. In the temperature range of 100–300 °C, the specimens charged with 712 ppm H and below show no significant change in RA, while those charged with 832 ppm H, tested at the same temperature range, display a significant drop in the RA. It may imply that the decrease in ductility may appear for the specimens containing 832 ppm H and above at temperatures from 100 to 300 °C. At the testing temperature 400 °C, there is no obvious variation in the RA over the entire range of hydrogen concentrations.

The increase in hydrogen contents may cause the slight increase in UTS and YS of Zry-4 specimens (Fig. 2 and Fig. 3). This suggests that over the entire range of hydrogen content from 0 to 832 ppm H, the strength is not significantly affected by the hydrides that precipitated in the matrix. As the temperature increases, the strength (YS and UTS) of Zry-4 decreases. In general, the decrease in strength is close to 70% from 25 to 400 °C. A

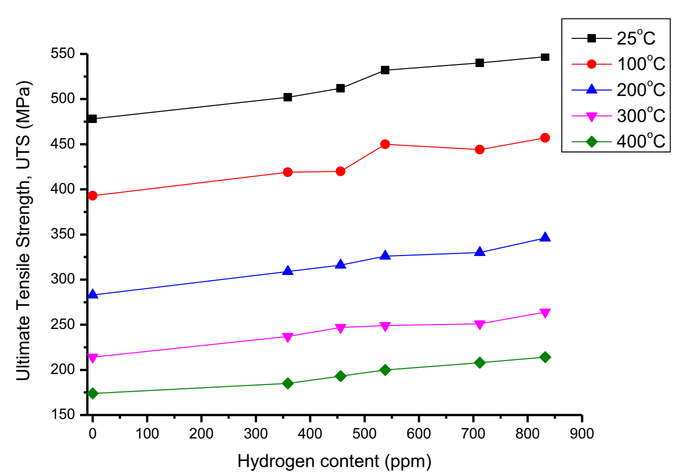

Fig. 2. Effect of hydrogen content on the ultimate tensile stress of Zircaloy-4 specimens at five temperatures.