MEASUREMENT OF FRACTURE TOUGHNESS OF HYDRIDED ZIRCALOY - 4

M. D. Callaghan¹, W.Y. Yeung¹, M. I. Ripley², D.G. Carr²

¹Department of Chemistry, Materials and Forensic Science, University of Technology, Sydney, P.O. Box 123, Broadway NSW 2007, Sydney, Australia.
²Materials and Engineering Science, Australian Nuclear Science and Technology Organisation, Private Mail Bag 1, Menai NSW 2234, Sydney, Australia.

ABSTRACT

Zircaloy-4 is a zirconium alloy that will be used for construction of many of the core components in the replacement research reactor at Lucas Heights. The fracture toughness of the alloy and its radiation-induced reduction over the 40 year planned life of the reactor is an important mechanical property for this application. This study aims to simulate the radiation-induced reduction in fracture toughness by hydriding Zircaloy-4. A range of fracture toughnesses is required to calibrate the sub-size Charpy and small punch (SP) surveillance specimens that will be irradiated over the life of the reactor against standard Jₑc fracture toughness specimens. Pieces of Zircaloy-4 plate were hydrided in a vessel at a temperature of 520°C, at different pressures for either 10 or 22 hours. Final hydrogen concentrations between 25 wt% ppm and 380 wt% ppm hydrogen were obtained under gaseous atmosphere. The fracture toughness of the hydrided Zircaloy-4 was assessed using sub-size 2.5 mm-thick Charpy, three-point bend Jₑc and SP tests. The results were correlated to determine the relationship between the J-integral fracture toughness, Charpy impact energy and equivalent fracture strain (εₑqf) from the SP tests. It was found that as hydrogen concentration and hydride formation increased, the fracture toughness of the alloy generally decreased. The results show there to be a useful relationship between fracture toughness and εₑqf measured for the SP tests.

1. INTRODUCTION

During the service life of nuclear reactors, embrittlement of zirconium alloys used in reactor core components occurs as a result of fast neutron irradiation. Zircaloy-4 (Zr-4) is to be used in ANSTO’s replacement research reactor (RRR) for reactor core components, including reflector vessel, beam tubes and chimney. The fracture toughness of this alloy is an important mechanical property to be studied over the service life of the reactor as embrittlement of Zircaloy will detrimentally affect mechanical properties and performance of components.

At present there is no irradiation embrittlement data for Zr-4 at RRR operating conditions. Hydrides are well known to cause embrittlement and reduce mechanical properties in zirconium alloys¹⁻³. Therefore hydride embrittlement could be used as a surrogate embrittlement process to obtain various Jₑc fracture toughness values, in order to obtain correlations between Jₑc fracture toughness and Charpy v-notch impact and SP tests.

There is a very limited volume available for surveillance specimens in the core of a nuclear reactor for analysis of radiation-induced changes and hydrogen absorption during service life. Jₑc fracture toughness and Charpy v-notch specimens use a large volume of material, whereas only small volumes of material are required for small punch specimens. The objective of this work was to define correlations between Jₑc fracture toughness and Charpy v-notch and SP tests in order to make better use of the limited volume available in the RRR for surveillance specimens.

2. MATERIAL AND EXPERIMENTAL PROCEDURE

2.1 Material

Test specimens were prepared from a hot rolled and annealed Zr-4 plate. Five Zr-4 pieces with dimensions 90 mm length, 90 mm width and 8.6 mm thickness were cut from the Zr-4 plate.

2.2 Hydrogen charging

Four Zr-4 pieces were gaseous hydrogen charged in a vessel using pure hydrogen at a temperature of 520°C, for either 10 or 22 hrs at pressures of 0.5, 0.67 and 1.0 atm. The pieces were furnace-cooled to room temperature inside the vessel after charging. Hydrogen concentrations between 25 wt% ppm and 380 wt% ppm hydrogen were achieved. A LECO™ hydrogen analyser was used to measure hydrogen concentration.

2.3 Test specimens

Test specimens for tensile, Charpy v-notch impact, fracture toughness and SP tests were prepared from each Zr-4 piece. Specimens were oriented transverse to the rolling direction of the Zr-4 plate. Tensile specimens were stamped to dimensions: length = 65
mm, width = 4 mm and thickness = 1 mm. Sub-sized 2.5 mm Charpy v-notch impact specimens were wire-cut to dimensions according to AS 1544.5-1981. Three point bend JIC specimens were wire-cut to dimensions: width (W) = 17.2 mm, thickness (B) = 8.6 mm in accordance with ASTM 1820-99a. The JIC specimens were fatigue pre-cracked to a crack length, a0 = 0.6W. The SP specimens were initially wire-cut with dimensions: 10 mm diameter and 0.6 mm thickness. The SP specimens were ground to a final thickness of 0.500 mm ± 0.005 mm.

2.4 Experimental procedure

Tensile testing was conducted according to AS 1391-1991, Charpy v-notch testing was conducted according to AS 1544.5-1981 and JIC testing was performed by evaluating J-R curves by the single-specimen unloading compliance technique on three point bend specimens, according to ASTM E1820-99a. SP testing was done using position control with a strain rate of 0.2 mm/min. All mechanical testing was done at room temperature.

2.5 Metallography and fracture analysis

Specimens were hot mounted in clear resin and a standard mechanical polishing procedure carried out, using Kemlube as lubricant. Final chemical polishing using the solution in Table 1 was done to reveal hydrides in the Zr-4 structure.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Peroxide (30%)</td>
<td>25 mL</td>
</tr>
<tr>
<td>Nitric acid (70%)</td>
<td>25 mL</td>
</tr>
<tr>
<td>Hydrofluoric acid (48%)</td>
<td>8-10 drops</td>
</tr>
</tbody>
</table>

Table 1. Chemical polishing solution.

Polished specimens were examined using optical microscopy to investigate and compare the amount of hydride formation and hydride orientation.

Scanning electron microscopy (SEM) analysis was used to observe both hydrides and fracture surfaces of JIC, Charpy v-notch and SP specimens. The SEM analysis was used in backscattered mode to observe hydrides and in secondary electron mode to observe hydrides and fracture surfaces.

3. RESULTS AND DISCUSSION

3.1 Hydride formation

Optical microscopy and SEM revealed that hydrides with platelet morphology formed in the Zr-4 microstructure and confirmed previous research on hydride platelet formation by slow furnace cooling after hydrogen charging. Hydride platelets formed uniformly throughout specimens and were intergranular and preferentially oriented parallel to the rolling direction of the plate. Hydride platelet band formation was observed parallel to the rolling direction of the 208 wt% ppm and 380 wt% ppm specimens and was thought to be due to low nucleation rates of hydrides and high diffusivity at slow cooling rates confirming the work of Hong et al. The amount of hydride platelets increased with increasing hydrogen concentration, but their size was found to be similar for all hydrogen-charged pieces. Hydride platelet thicknesses were approximately 1 µm, platelet lengths varied but were generally less than 25 µm. The hydride platelet dimensions at slow furnace cooling rates were similar to those found by Bai et al.

Figure 1. Optical micrograph of hydride platelets and banding in a 380 wt% ppm specimen at x200.

3.2 Mechanical testing

3.2.1 Charpy v-notch

The results of Charpy v-notch tests are shown in Figure 2. They show that the absorbed impact energy decreased exponentially with an increase in hydrogen concentration. The decrease in absorbed impact energy with increased hydrogen concentration is due to hydride embrittlement.

Figure 2. Average absorbed energy vs Hydrogen concentration.

3.2.2 JIC

All JIC specimens displayed stable crack extension as can be seen in Figure 3, which gives representative
graphs of load versus crack opening displacement. Ductility, load and crack opening displacement reduced with increasing hydrogen concentration due to hydride embrittlement.

The variation in fracture toughness with hydrogen concentration is shown in Figure 5. An exponential decrease in fracture toughness was observed and is in agreement with the results reported by Kreyns et al\(^2\).

3.2.3 Small punch

Representative load versus deflection graphs for SP specimens are shown in Figure 6. Regions of crack initiation, measured visually during testing, are shown by circles on the graph. The load and deflection decreased as hydrogen concentration increased, consistent with hydride embrittlement.

The specimens with lower hydrogen concentration displayed ductile behaviour characterised by the three small punch deformation regimes described by Mao et al\(^9\). The specimens with higher hydrogen concentrations displayed only plastic bending due to the significant reduction in ductility caused by hydride embrittlement. No evidence of membrane stretching was seen in these specimens. Due to hydride embrittlement, lower failure loads were observed in specimens containing higher hydrogen concentrations.
A value of the equivalent fracture strain, $\varepsilon_{qf}$, may be calculated according to the following empirical relation:

$$\varepsilon_{qf} = \ln \left( \frac{t_0}{t} \right) = \beta \left( \frac{\delta}{t_0} \right)^x$$

- $t_0$ = initial thickness of SP specimen
- $t$ = minimum thickness of fractured specimen
- $\beta$ = a constant
- $x$ = a constant
- $\delta$ = maximum deflection occurring at the fracture load ($P_T$).

The parameters $\beta$ and $x$ were calculated from the linear regression between $\ln \ln \left( \frac{t_0}{t} \right)$ and $\ln \left( \frac{\delta}{t_0} \right)$ in accordance to the method of Misawa et al.\textsuperscript{10}.

![Graph showing the relationship between ln(ln(t₀/t)) and ln(δ/t₀) for Zr-4 SP specimens.](image)

**Figure 7.** A graph showing the relationship between $\ln \ln \left( \frac{t_0}{t} \right)$ and $\ln \left( \frac{\delta}{t_0} \right)$ for Zr-4 SP specimens.

A linear correlation (Figure 7.) was obtained with an $R^2$ value of 0.9791. The empirical parameters were calculated to be $\beta = 0.17081$ and $x = 1.0675$ and $\varepsilon_{qf}$ values were determined. Other researchers\textsuperscript{9-12} have found good correlations between $\varepsilon_{qf}$ and fracture toughness for other materials and correlations in the present work with $J$-integral fracture toughness are presented in 3.4.

### 3.3 SEM

The fracture surface analysis of Charpy, $J_{IC}$ and SP specimens showed that, despite the apparently brittle behaviour with increasing hydrogen concentration, the as-received and hydrogen-charged specimens fractured in a ductile manner as evidenced by dimple rupture morphology (Figures 8, 10, 11). Cracks and associated cleavage facets around crack regions (Figure 9.), characteristic of brittle fracture, were observed in the hydrogen-charged specimens. These sites correspond to sites of crack propagation at brittle hydride platelets\textsuperscript{13}. Fracture surface analysis confirmed that embrittlement of Zr-4 is due to the presence of hydride platelets; fracture occurs by linking up of brittle cracks in the hydride platelets after crack initiation and by ductile fracture of the intervening matrix as proposed by Huang and Huang\textsuperscript{14}. Our work showed that the fracture path followed the hydride platelet network as proposed by Bai et al.\textsuperscript{13} and Bertolino et al.\textsuperscript{1}. The number and size of cracks was observed to increase with increasing hydrogen concentration.

![SEM micrograph of the crack extension region of a 31 wt% ppm $J_{IC}$ fracture toughness specimen at x1000. Dimple morphology and cracks are seen.](image)

**Figure 8.** SEM micrograph of the crack extension region of a 31 wt% ppm $J_{IC}$ fracture toughness specimen at x1000. Dimple morphology and cracks are seen.

![SEM micrograph of the region around the crack of a 31 wt% ppm $J_{IC}$ fracture toughness specimen at x4000. Cleavage facets can be seen in and around the crack.](image)

**Figure 9.** SEM micrograph of the region around the crack of a 31 wt% ppm $J_{IC}$ fracture toughness specimen at x4000. Cleavage facets can be seen in and around the crack.

![SEM micrograph of the fracture surface of 208 wt% ppm Charpy v-notch specimen at x1000. Dimple morphology and cracks are seen.](image)

**Figure 10.** SEM micrograph of the fracture surface of 208 wt% ppm Charpy v-notch specimen at x1000. Dimple morphology and cracks are seen.
Figure 11. SEM micrograph of the fracture surface of 25 wt% ppm SP specimen at x500. Elongated dimples can be seen.

When greater amounts of brittle hydride platelets are present in the material, a continuous hydride platelet network occurs leading to an increase in brittle fracture. The network provides a continuous path for crack propagation after crack initiation. The brittle nature of hydride platelets results in a decrease in ductility and strength of the overall Zr-4-hydride matrix and therefore a reduction in fracture toughness.

3.4 Mechanical property correlations

The major objective of the work was to develop mechanical property correlations. These are presented in this section.

3.4.1 J-integral – absorbed impact energy

$J_{IC}$ fracture toughness testing gave values of $J_{IC}$ and $J_Q$ and so separate correlations were made with the Charpy v-notch results. The linear best fits to each (i.e. $J_{IC}$ and $J_Q$) are given in Figure 12.

J-integral fracture toughness vs absorbed impact energy

From the linear correlations between $J_{IC}$ and $J_Q$ fracture toughness versus average $\varepsilon_{qf}$ values.

From the linear correlations between $J_{IC}$ and $J_Q$ fracture toughness and $\varepsilon_{qf}$, the following relationship is obtained:

$$J_{IC} = k\varepsilon_{qf} - J_0 \text{ and } J_Q = k\varepsilon_{qf} - J_0$$

Where $k$ and $J_0$ are materials/environmental dependent constants presented in Table 2.

Table 2. Materials/environmental constants.

<table>
<thead>
<tr>
<th>Correlation</th>
<th>K (kJ/m²)</th>
<th>$J_0$ (kJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_{IC}$</td>
<td>112.9</td>
<td>25.9</td>
</tr>
<tr>
<td>$J_Q$</td>
<td>569.0</td>
<td>32.4</td>
</tr>
</tbody>
</table>

For the correlations between J-integral fracture toughness, absorbed impact energy and $\varepsilon_{qf}$, the following must be noted. $J_0$ is a size dependent measure of fracture toughness and thus the $J_Q$ versus absorbed impact energy or $\varepsilon_{qf}$ correlation is a size dependent correlation. For structural integrity analysis, using the same specimen size only (8.6 mm thickness for $J_{IC}$ specimens), the $J_Q$ versus absorbed impact energy or $\varepsilon_{qf}$ correlations may be used. $J_{IC}$ is a size independent measure of fracture toughness and thus the $J_{IC}$ versus absorbed impact energy or $\varepsilon_{qf}$ correlation are size independent correlations. For size independent structural integrity analysis, the $J_{IC}$ versus absorbed impact energy or $\varepsilon_{qf}$ correlations may be used.
4. CONCLUSIONS

Hydriding Zr-4 to concentrations between 25 wt% ppm and 380 wt% ppm hydrogen was achieved by gaseous hydrogen charging.

The mechanical properties including J-integral fracture toughness, Charpy absorbed impact energy and $\varepsilon_{ql}$ from the SP tests decreased when hydrogen concentration and subsequent hydride formation was increased in the Zr-4.

Fracture surface analysis revealed that specimens fractured in a ductile manner as evidenced by dimple rupture morphology. Cracks and associated cleavage facets around crack regions correspond to sites of crack propagation at brittle hydride platelets and fracture occurs by linking up of brittle cracks in the hydride platelets after crack initiation.

Linear correlations between J-integral fracture toughness and (i) absorbed impact energy from Charpy v-notch impact testing and (ii) equivalent fracture strain ($\varepsilon_{ql}$) from SP testing were obtained. These correlations enable the use of smaller volume test specimens in estimating the in-service structural integrity of Zr-4 reactor core components.

ACKNOWLEDGMENTS

The authors would like to thank Mr Graham Smith for assistance in metallography, Mr Paul Stathers for assistance in hydrogen charging, Mr Sam Humphries for guidance in mechanical testing and Dr Huijin Li for assistance in SEM analysis.

REFERENCES