Development of Gaseous Hydrogen Charging of Zr Alloys Using A Coulometric Titration Technique

M. Saoudi, J. Mouris and Z. He
Atomic Energy of Canada Limited, Chalk River Laboratories, Chalk River, Ontario,
Canada K0J 1J0

Abstract

The Coulometric titration technique is described and shown as a variant of the gaseous hydriding method. Zircaloy-4 samples were hydrided by exposure to ultrahigh purity argon gas containing up to 7500 ppm hydrogen in a quartz-tube furnace at 400°C. At known temperature and hydrogen partial pressure, the sample hydrogen uptake is controlled by the exposure time to the gas. This technique has been successfully used at Chalk River Laboratories to charge mechanical test specimens of Zircaloy-4 to high levels of hydrogen concentration, with adequate control of hydrogen uptake, with uniform distribution of the hydride phase and without extraneous changes to alloy microstructure.

1. Introduction

The mechanical properties of Zircaloy fuel cladding are affected by the presence of hydrides. Because of its technological importance, hydrogen embrittlement of Zircaloy has been studied extensively [1, 2].

In the last few years, fuel burnups have been gradually extended in order to reduce the amount of spent fuels and hence to reduce the overall fuel cost. When extending fuel burnups, corrosion and hydrogen pickup in Zircaloy fuel sheath gradually increase [3]. Therefore, characterisation of the effect of zirconium hydride on the mechanical behaviour of fuel cladding is important. Such research requires the controlled hydriding of experimental specimens. The objective of the present study was to develop a hydriding method, as part of sample preparation to conduct such research.

Historically, three methods have been used for hydriding zirconium alloy specimens: gaseous hydriding [4], electrolytic-anneal [5] and LiOH exposure [6]. Both, the second and third techniques involve difficulties in control of hydrogen uptake and a high probability of specimen surface damage [5, 6]. The first technique is widely used. Since hydrogen dissolution in the zirconium alloy follows Sievert's law quite rigorously [7], hydrogen concentration in the specimen can be controlled by controlling the hydrogen pressure.

In this paper we present a variant of the gaseous hydriding method using the coulometric titration (CT) technique. The purpose of this work is to charge mechanical test specimens of Zircaloy-4 to high levels of hydrogen concentration (above the hydrogen solubility limit), with uniform distribution of the hydride phase and without altering the specimen's original microstructure.

2. Experimental

2.1 Coulometric titration technique

The coulometric titration technique was successfully used at Chalk River Laboratories to measure the O/M ratio (oxygen to metal ratio) of UO_2 samples in defected fuels [8-9]. In the present work we used the CT equipment to conduct gaseous hydrogen charging of Zircaloy-4 specimens. The basic operation of the CT equipment in this mode is shown schematically in Figure 1. The CT equipment mainly consists of three components: an upstream CT cell, a reaction furnace, and a downstream CT cell. A detailed description of the working principle of the ceramic CT cell is given in [8-9]. Initially, ultra high purity Ar gas containing a constant and known quantity of H_2 (varying from 2000 to 7500 ppm) flows through the upstream CT cell and passes over the sample into the reaction furnace and then into the downstream CT cell. The upstream and downstream CT cells are heated at 750°C, but not the sample furnace. At room temperature no reaction between the sample and gas occurs. This initial step allows the purging of the sample space to a very low level of oxygen. It allows also establishing the baseline for the titration current peak (see Figure 2).

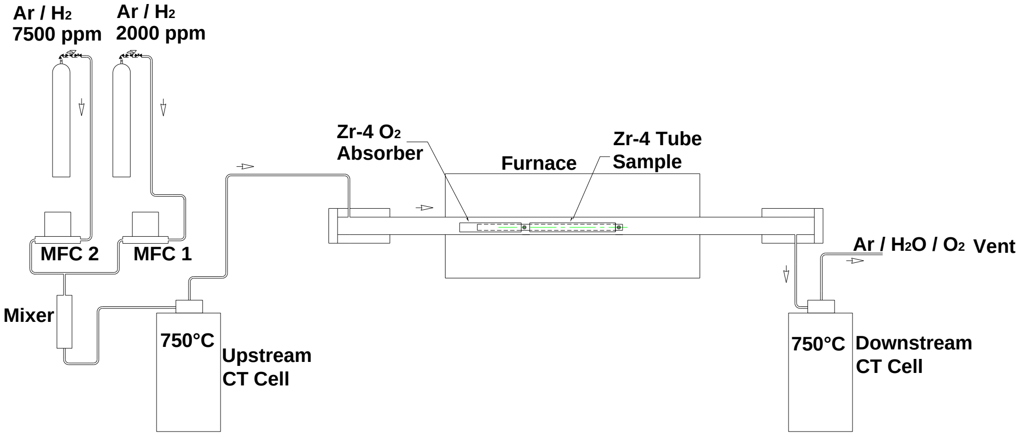

Figure 1 Schematic Diagram of Coulometric Titration Apparatus for Gaseous Hydrogen Charging.

In the downstream cell, just enough oxygen is added to convert all the H_2 to H_2O. The oxygen is added by passing a current of oxygen ions from the surrounding air through the ceramic cell wall at 750°C into the gas. The composition of the gas in the downstream CT cell is continually monitored, and a feedback loop continually adjusts the current in order to supply the precise amount of oxygen that is necessary to convert all H_2 to H_2O. For this reason, the current is termed the titration current. Figure 2 shows the results of gaseous hydrogen charging of a Zircaloy-4 cladding tube specimen. The titration current in this figure represents the amount of oxygen ions needed in the downstream CT cell to exactly convert all the H_2 to H_2O.

As the Zircaloy-4 sample heats up in the furnace, the sample absorbs hydrogen. Since a chemical equilibrium ($2H_2 + O_2 = 2\ H_2O$) is maintained via the temperature of the furnace, the downstream cell adds a controlled amount of O_2 from the outside atmosphere to convert the remaining H_2 (not absorbed by the sample) to H_2O. Therefore, the amount of O_2 required in the downstream cell to combine with the remaining H_2 is now decreased and shows as a drop of the titration current from the baseline (see Figure 2). This difference in the amounts of O_2 (between the initial amount at room temperature and the decreased amount) is measured and integrated, which controls the hydrogen uptake in the sample as function of the exposure time of the sample to the gas under a constant hydrogen partial pressure. The integrated value can then be calculated to obtain the total amount of hydrogen absorbed by the sample.

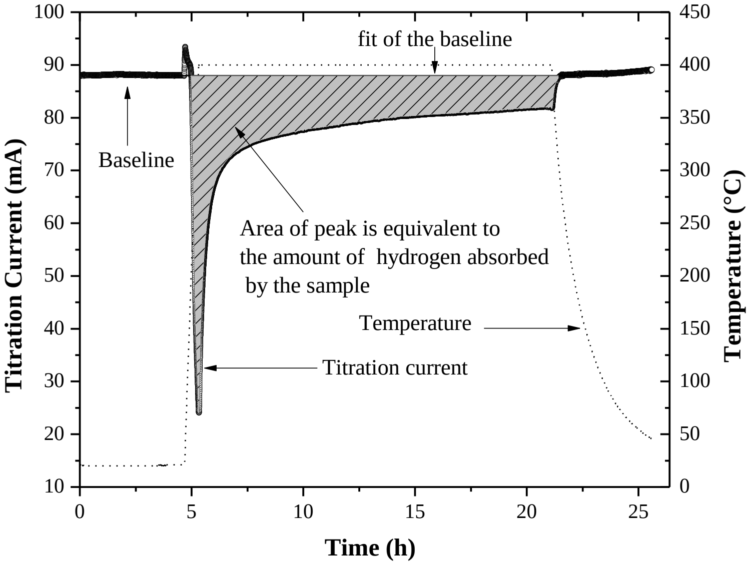

Figure 2 Gaseous Hydrogen Charging of a Zircaloy-4 Specimen in Ar Gas Containing 4000 ppm H_2 at 400°C. The dotted line represents the temperature profile and the solid line is the fit of the experimental measured baseline.

2.2 Sample preparation

Samples were cut from cold rolled and stress relieved Zircaloy-4 cladding tube and sheet materials and were individually hydrided using the CT equipment described in Section 2.1. Plate specimens were 10 mm × 20 mm ×1.6 mm and tube specimens were 120 mm long. Prior to the hydriding charge, the surface of the specimen was cleaned to ensure uniform hydrogen charging. To remove the oxide layer, the specimen was polished with a series of abrasive papers up to 600 grit and then cleaned with wipes. The cleaned sample was weighed and immediately put into the quartz tube in the CT equipment furnace next to an oxygen absorber in order to avoid surface oxidation of the sample and promote hydrogen uptake during charging. After hydrogen charging at 400°C, the sample was furnace cooled to room temperature.

In order to obtain a uniform hydride distribution throughout the thickness of the samples, a homogenization heat treatment in argon gas atmosphere for 10 hours was applied. The H-Zr equilibrium diagram presents a eutectoide transformation at ~ 550 ^{o}C [10]. To avoid both the phase transformation and the alteration of the original microstructure of samples, the homogenization temperature was lower than 550^{o}C and higher than the dissolution temperature [11]. The samples were furnace cooled to room temperature. The slow cooling rate used is aimed at avoiding formation of γ hydrides.

2.3 Hydrogen analysis

Hydrogen analysis consists of hydrogen uptake measurements and characterisation of the hydride distribution, orientation and morphology throughout the sample by metallographic analysis. The absorbed hydrogen content in the specimens was measured by a hot vacuum extraction mass spectrometry system (HVEMS). The hydride dissolution temperature of the specimens was evaluated with Differential Scanning Calorimetry (DSC). The phase transition temperatures were measured for two runs. The runs consist of a cooldown to ambient temperature from some maximum temperature, followed by a heat-up to the same maximum temperature with a hold time of 5 min. The hydrogen-charged samples were optically examined for hydride distribution using standard metallographic procedures. The specimen for hydrogen analysis was cut into three sections from three different locations as shown in Figure 3. The hydrogen concentration of each specimen was calculated as the mean of such measurements for at least three sections from the specimen in question.

X-ray diffraction measurements were also performed at room temperature using CuKα radiation to analyse the existing phases in the specimens using a scan step size of 0.010°.

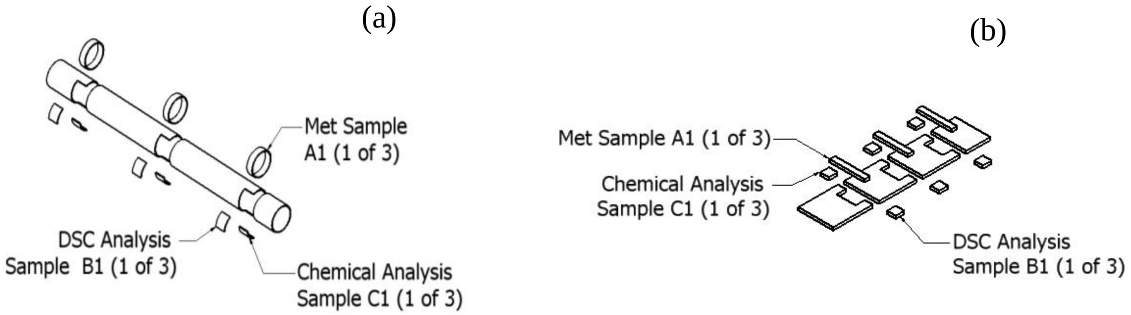

Figure 3 Cutting Diagram of Zircaloy-4 Cladding Tube (a) and Sheet Material (b) for Metallographic Examination, DSC Examination and HVEMS.

3. Experimental results

3.1 Hydrogen uptake measurements

The integrated area of the titration current peak shown in Figure 2 is equivalent to the amount of absorbed hydrogen by the sample. In order to calibrate the integrated area for a given time exposure of the sample to gas under a known temperature and hydrogen partial pressure, the samples were analyzed for hydrogen concentration by HVEMS. Their hydrogen contents range from 15 to 390 ppm (by weight), and the statistical errors were within 2%.

As shown in the cutting diagram in Figure 3, the hydride dissolution temperature of the samples cut from plate and tube specimens was evaluated by DSC in the temperature range from 217 to 488ºC. Figure 4 shows a representative DSC curve. The temperature at the peak of the derivative heat flow curve, 460°C, is the hydride dissolution temperature of the sample. These temperatures are summarized in Figure 5 as the terminal solid solubility dissolution (TSSD) of the hydrides for the analyzed specimens. Figure 5 shows the measured hydrogen content C_H by HVEMS, including the uncertainties of the hydrogen measurements, and the corresponding TSSD evaluated by DSC.

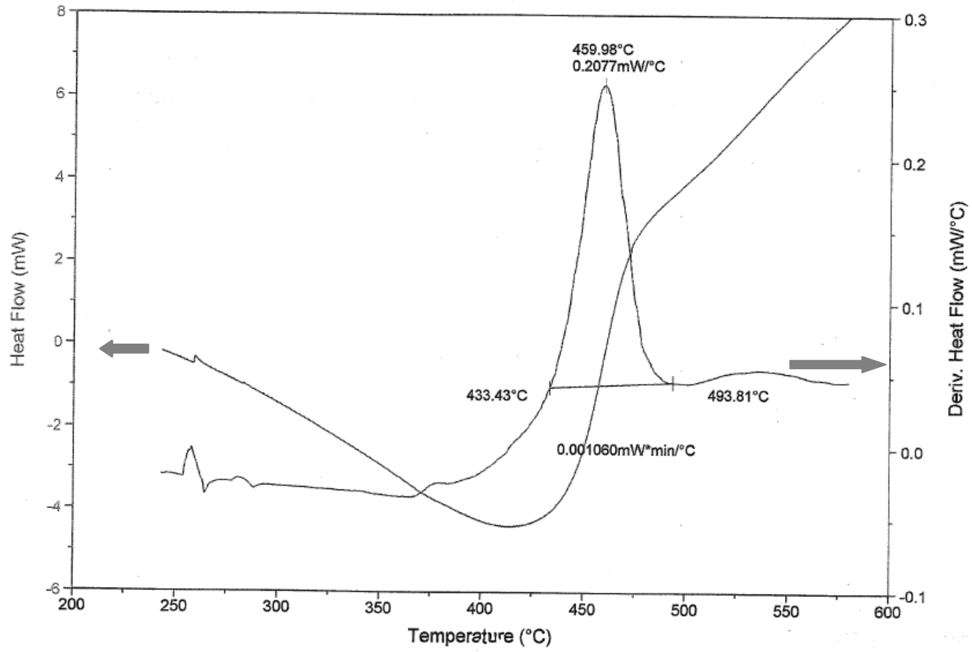

Figure 4 DSC Data of a Zircaloy-4 Sheet Specimen with a Nominal Hydrogen Content of 300 ppm.

The TSSD shows a linear relation of $\ln C_H$ versus 1/T and can be fitted using the Van't Hoff's equation [12]

$$C_H = A \exp(-Q/RT) \qquad (1)$$

Where C_H, A, Q ($J\ mol^{-1}$), R ($8.314\ J\ K^{-1}\ mol^{-1}$) and T (K) are the hydrogen content, a constant related to the dissolution entropy, the dissolution enthalpy, the ideal gas constant and the absolute temperature, respectively. The fit parameters A and Q are given in the expression below

$$C_H = 115844 \exp(-36264.8/RT) \qquad (2)$$

The results are in good agreement with the data reported by Slattery between 30°C and 400°C [11] as shown in Figure 5.

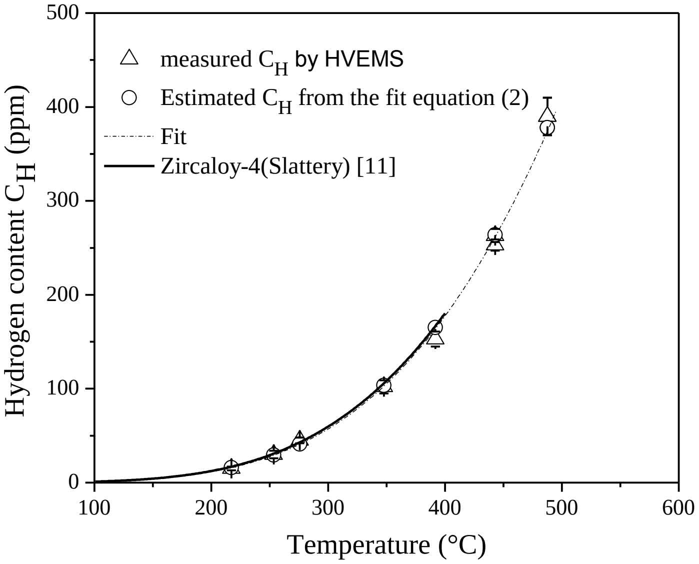

Figure 5 Hydrogen content C_H versus TSSD Temperature as Measured by DSC. The triangles are the measured hydrogen content by HVEMS, and the circles are the hydrogen content calculated using expression (2). The dashed line represents the fit to the experimental data.

Based on the DSC results, the reported values of hydrogen concentration using expression (2) were the average of at least three measurements as shown in the cutting diagram of Figure 3. The maximum scatter of several sections cut from the charged specimen was within ± 5% of the average. The reproducibility of this hydrogen charging technique was within ± 17% of the average of hydrogen content present in the sample.

3.2 Hydride characterisation

The charging uniformity was confirmed metallographically by examining the hydride distribution through the sample thickness from at least three different sections of the same sample. Figure 6 shows typical optical micrographs of uniformly distributed hydrides in an as-received Zircaloy-4 sheet specimen hydrided to 300 ppm. Hydride precipitates are platelet shaped, oriented in planes parallel to the rolling direction. The single peak in the heat flow response and its temperature derivative in Figure 4 also indicates a uniform distribution of hydrides in the matrix, which is in good agreement with the optical examination results.

As was expected from the slow cooling rate used, only δ precipitates were detected by X-ray diffraction. There was no evidence of precipitation of γ hydrides as shown in Figure 7.

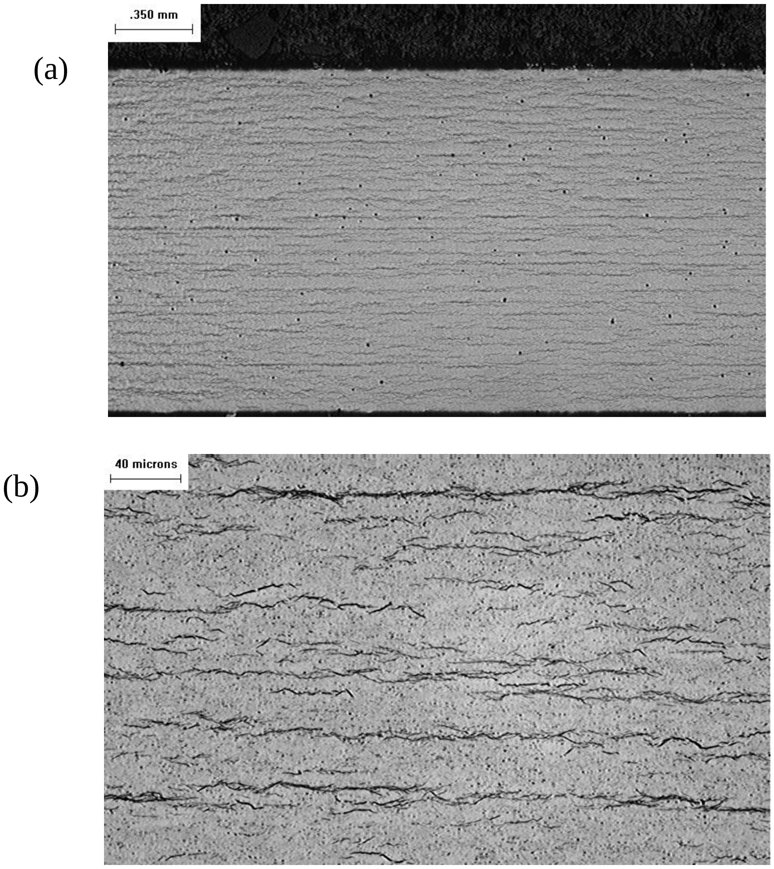

Figure 6 Optical Micrograph of Uniformly Hydrided As-Recieved Zircaloy-4 Sheet Specimen with Nnominal Hydrogen content of 300 ppm. (a) Low Magnification and (b) High Magnification.

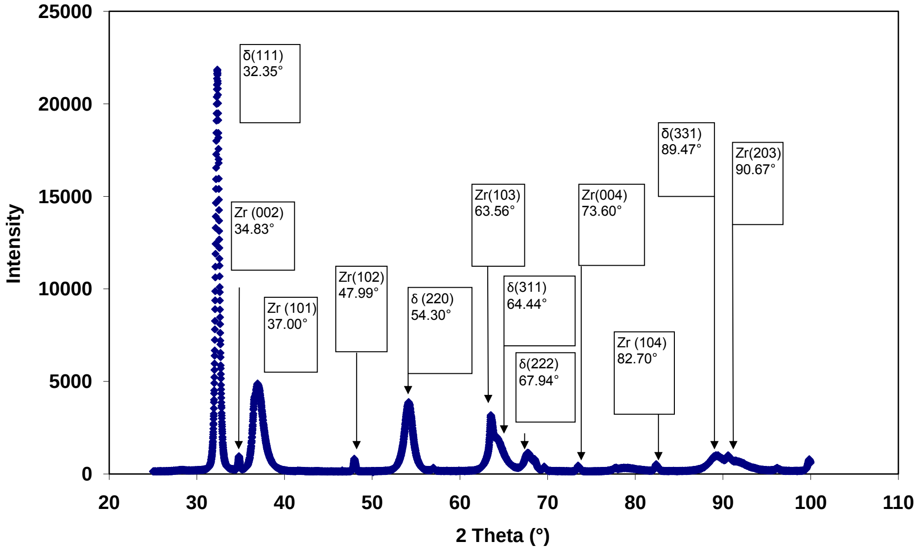

Figure 7 X-Ray Spectra of Zircaloy-4 Sheet Specimen Hydrided to a Nominal Hydrogen Content of 150 ppm.

4. Conclusion

We have developed a gaseous hydrogen charging method using the coulometric titration technique. The hydrogen charging employed produced the desired hydride precipitates of the δ phase type. To obtain a uniform hydride distribution over the specimen thickness, a low hydrogen partial pressure should be used to avoid the formation of hydride surface layers. Under appropriate test conditions, at known temperature and hydrogen partial pressure, the hydrogen uptake is controlled by time exposure of the sample to the gas. We have shown that this technique is appropriate for charging hydrogen into Zircaloy-4 to a concentration exceeding the hydrogen solubility limit with uniform distribution of the hydride phase and without alteration of the original microstructure of the samples.

Acknowledgement

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5. References

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