HYDROGEN CONCENTRATION DETERMINATION IN PRESSURE TUBE SAMPLES USING DIFFERENTIAL SCANNING CALORIMETRY (DSC)

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ABSTRACT

Zirconium alloys are widely used as a structural material in nuclear reactors.
It is known that zirconium based cladding alloys absorb hydrogen as a result of service in a pressurized water reactor.
Hydrogen absorbed (during operation of the reactor) in the zirconium alloy, out of which the pressure tube is made, is one of the major factors determining the life time of the pressure tube. For monitoring the hydrides, samples of the pressure tube are periodically taken and analyzed.
At normal reactor operating temperature, hydrogen has limited solubility in the zirconium lattice and precipitates out of solid solution as zirconium hydride when the solid solubility is exceeded.
As a consequences material characterization of Zr-2.5Nb CANDU pressure tubes is required after manufacturing but also during the operation to assess its structural integrity and to predict its behavior until the next in-service inspection.
Hydrogen and deuterium concentration determination is one of the most important parameters to be evaluated during the experimental tests.
Hydrogen present in zirconium alloys has a strong effect of weakening.
Following the zirconium-hydrogen reaction, the resulting zirconium hydride precipitates in the mass of material. Weakening of the material, due to the presence of 10 ppm of precipitated hydrogen significantly affects some of its properties.
The concentration of hydrogen in a sample can be determined by several methods, one of them being the differential scanning calorimetry (DSC). The principle of the method consists in measuring the difference between the amount of heat required to raise the temperature of a sample and a reference to a certain value. The experiments were made using a TA Instruments DSC Q2000 calorimeter.
This paper contains experimental work for hydrogen concentration determination by Differential Scanning Calorimetry (DSC) method. Also, the reproducibility and accuracy of the method used at INR Pitesti are presented.

Key words: DSC, zirconium alloys, Differential Calorimetry

Introduction

During operation of the reactor, the zirconium alloy, out of which the pressure tube is made, absorbed hydrogen. The quantity of the hydrogen is one of the major factors determining the life time of the pressure tube. For monitoring the hydrides, samples of the pressure tube are periodically taken and analyzed.

The design of **CANDU-PHWR** (Canada Deuterium Uranium – Pressurized Heavy Water Reactor) is based on about 400 individual channels, which hold the fuel bundles, comprising pressure tubes of Zr-2.5Nb alloy joined to stainless steel end-fittings, operating in an environment of heavy water at elevated temperature (250 to 300°C) and internal pressure (10MPa) in a fast neutron flux ($\cong 10^{17} n/m^2 s$).

As a consequences material characterization of Zr-2.5Nb CANDU pressure tubes is required after manufacturing but also during the operation to assess its structural integrity and to predict its behavior until the next in-service inspection. Hydrogen and deuterium concentration determination is one of the most important parameters to be evaluated during the experimental tests.

Methods for hydrogen concentration determination

Tree methods for hydrogen concentration determination in zirconium alloys are used for fuel cladding and other structural materials, namely:

- Inert Gas Fusion method;
- Differential Scanning Calorimetry (DSC)
- High Vacuum Extraction Mass Spectrometry.

High Vacuum Extraction Mass Spectrometry method consists of gases extraction by heating under vacuum and analysis by mass spectrometry. This method is useful for heavy water cooled reactors. It has the ability to separate hydrogen and deuterium in order to establish the content of hydrogen in the zirconium alloys as received and the deuterium absorbed during the operating. Unfortunately, this method is very complex end difficult to apply especially for irradiated materials.

The most widely used method for hydrogen determination in zirconium alloys is Inert Gas Fusion method. Sample is melting in a furnace and hydrogen content is transferred by means of a carrier gas in a Thermal Conductivity Detector.

The principle of the Differential Scanning Calorimetry (DSC) method consists in measuring the difference between the amount of heat required to raise the temperature of a sample and a reference to a certain value. The experiments were made using a TA Instruments DSC Q2000 calorimeter (**Figure 1**).

The DSC method is used to estimate the amount of the hydrogen dissolved in the sample, and also to estimate the precipitation temperature. As presented in ref. [1], the terminal solid solubility of hydrogen in Zircaloy C_H has previously been measured and is given by the relation $C_H = A \exp(-E_H/T)$ where A is a constant, equal to 1.2×10^5 wt. ppm, and E_H is the difference between the partial molar heat of solution of hydrogen in solid solution and partial molar heat of solution of hydrogen in hydrides. A TA Instruments Q2000 MDSC was used for experimental measurements. The instrument was specially designed with detachable furnace in order to be used also for radioactive materials and has the following specifications: Sensitivity: <0.2 µW; Discovery Finned Air Cooling System; Operating temperature range: Ambient to 725°C; Temperature accuracy: ± 0.1°C; Baseline Curvature (50 to 300°C): <0.15 mW; Baseline Reproducibility with Tzero: ±10µW; Heating rate: 0.01 to 100 °C/min; Cooling rate: 0.01 to 20 °C/min.

A key contributor to the quality of DSC results is the sample preparation. The new Tzero® DSC Sample Encapsulation Press (**Figure 2**) takes sample encapsulation to a higher level of performance and convenience in conventional and hermetic sealing of a wide variety of materials. The press kit includes die sets for the new Tzero aluminum and Tzero hermetic pans & lids.

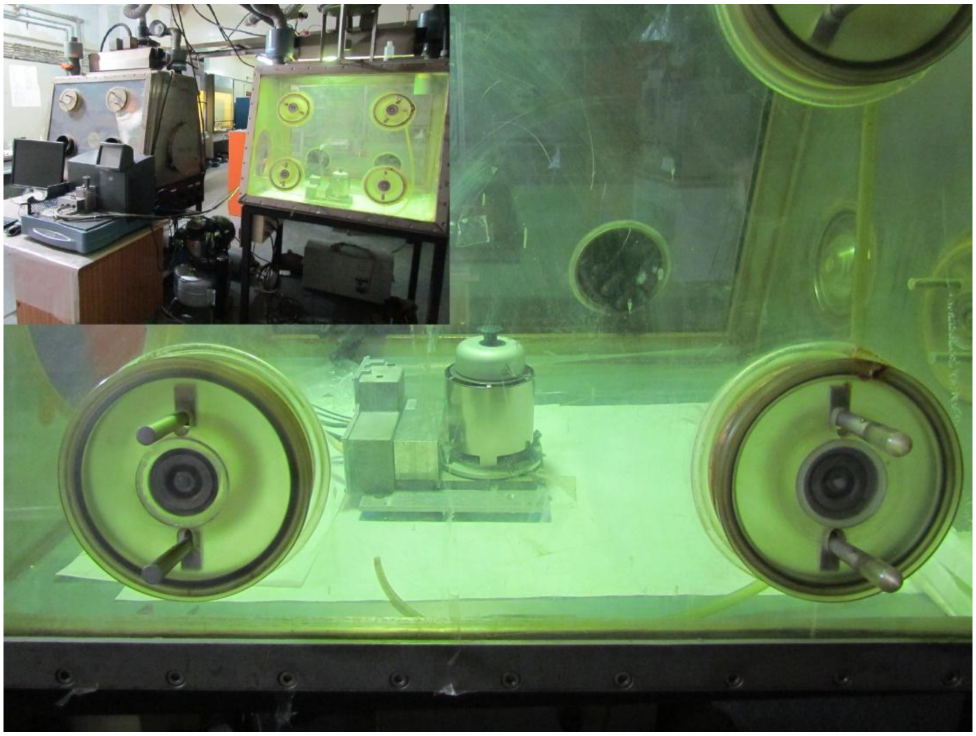
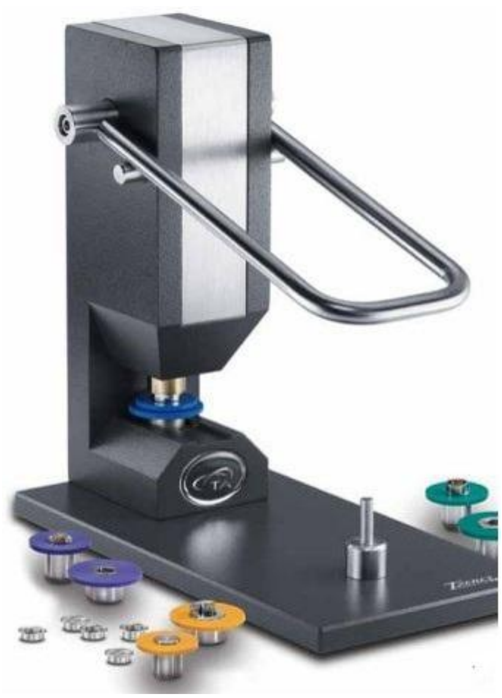


Figure 1 *Differential Scanning Calorimeter* **-***TA Instruments Q2000*



Equipment used and required materials

- Differential Scanning Calorimeter –TA Instruments Q2000 MDSC with detachable furnace instaled in the hot cell (**Figure 1)**;
- Tzero aluminum pans & lids (**Figure 2**);
- Tzero® DSC Sample Encapsulation Press and accesories compatible with Tzero aluminium pans (**Figure 2**);
- Nitrogen cylinder with pressure regulator;
- Air compressor for furnace cooling;
- Tweezers for remote handling in hot cell;
- Dedicated scissors for scrape sample cutting.

Figure 2 *Tzero® DSC Sample Encapsulation Press and accessories*

Working method

For the experimental work, the samples have to be prepared first for the encapsulation. After cutting, the samples are washed in alcohol, and then embedded in Tzero aluminium pans using Tzero® DSC Sample Encapsulation Press.

The sample encapsulated in Tzero aluminium pan is placed on the sample sensor and an encapsulated empty Tzero aluminium pan with lid is used as reference (**Figure 3**)

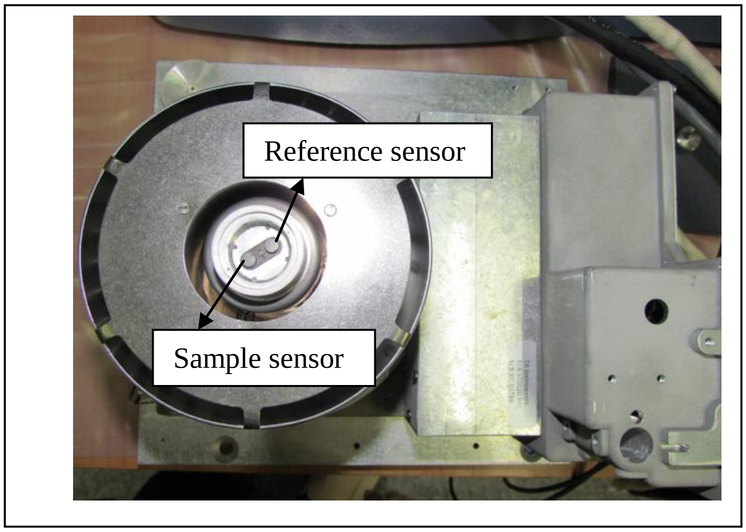


Figure 3 *Position of the reference sensor and the sample sensor*

For better accuracy, at least 3 measurement cycles have to be performed.

In order to demonstrate the reproducibility and accuracy of the DSC method, three samples of pressure tube (Zr-2.5Nb) with known hydrogen concentration were annealed (Sample 1 – Zr-2.5Nb, mass: 45 mg, hydrogen concentration: 30 ppm; Sample 2 – Zr-2.5Nb, mass: 28.13 mg, hydrogen concentration: 60 ppm; Sample 3 – Zr-2.5Nb, mass: 32.27 mg, hydrogen concentration: 100 ppm)
In figures below are presented the spectra obtained for the samples.

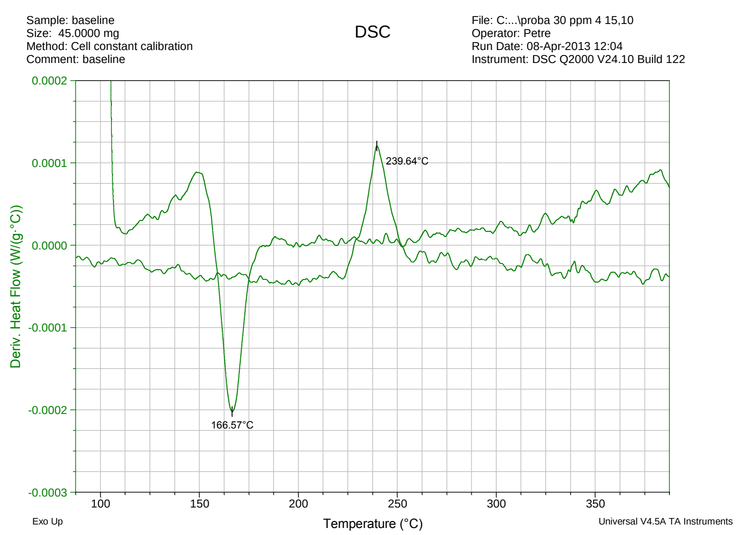


Figure 4 *Deriv. Heat flow of sample 1*

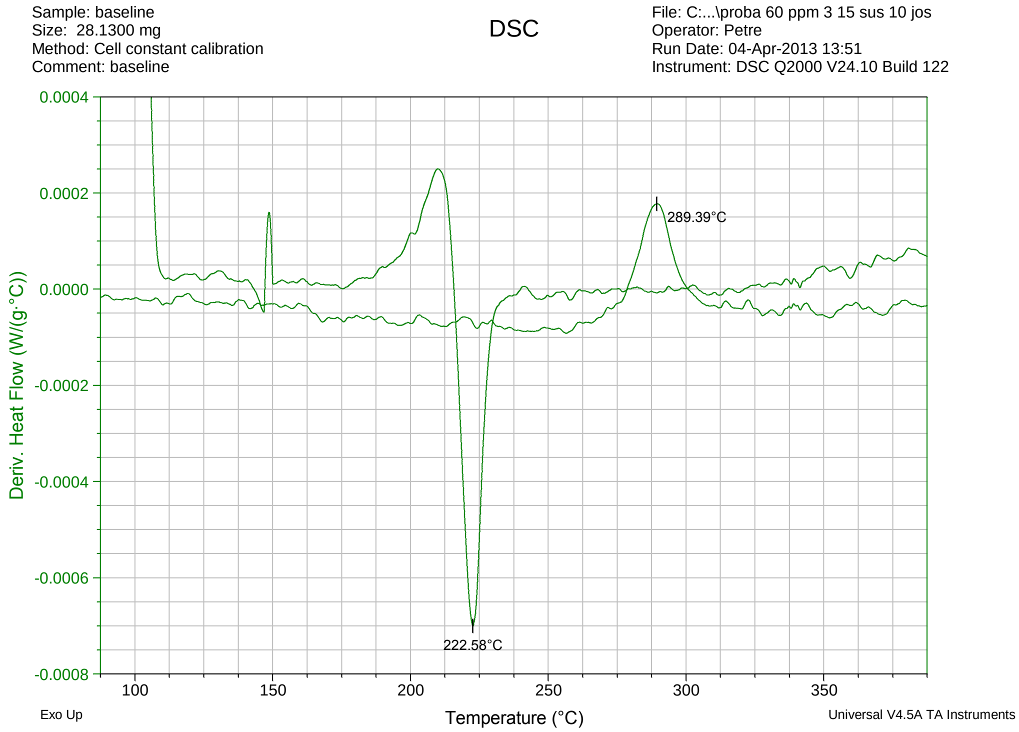


Figure 5 *Deriv. Heat flow of sample 2*

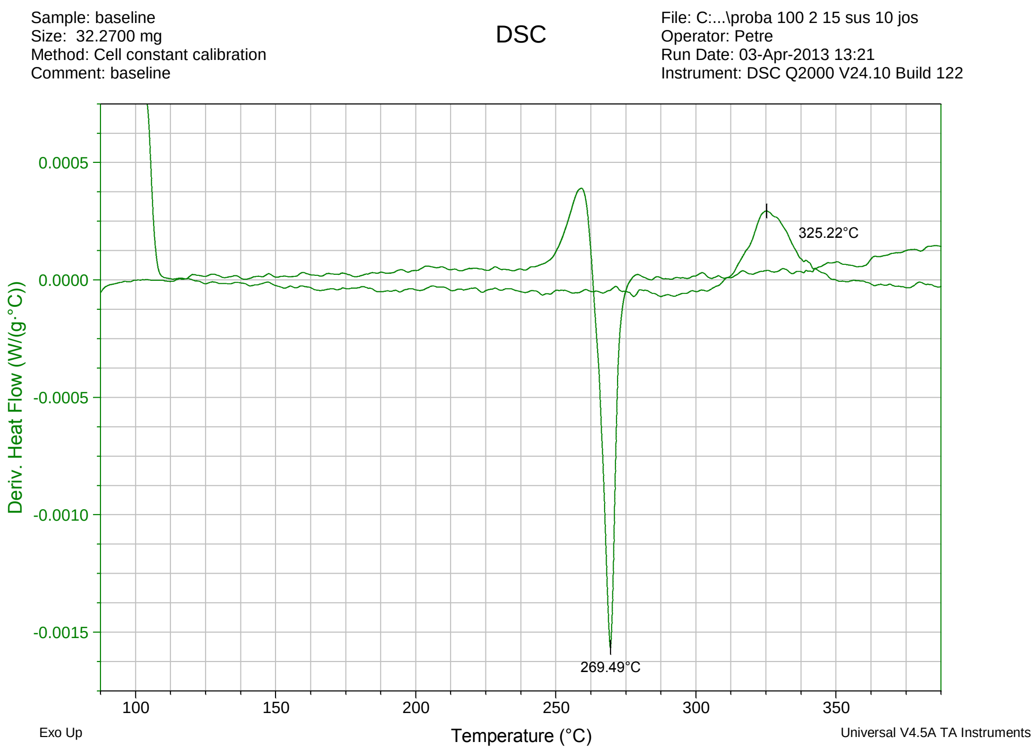


Figure 6 *Deriv. Heat flow of sample 3*

In **Figures 7 and 8** are presented in detail the Terminal Solid Solubility during the Dissolution (TSSD) and the Terminal Solid Solubility during the precipitation (TSSP) peaks for four sequentially measurements for sample 2. We can see that the peak position is also reproducible with a precision less than ±1°C.

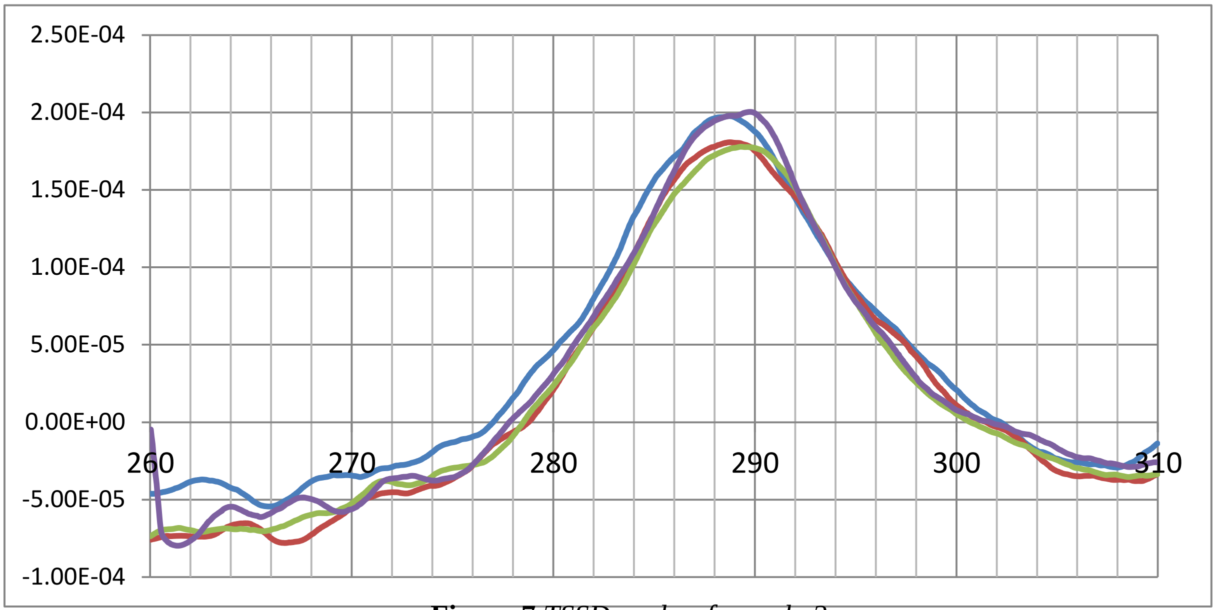


Figure 7 *TSSD peaks of sample 2*

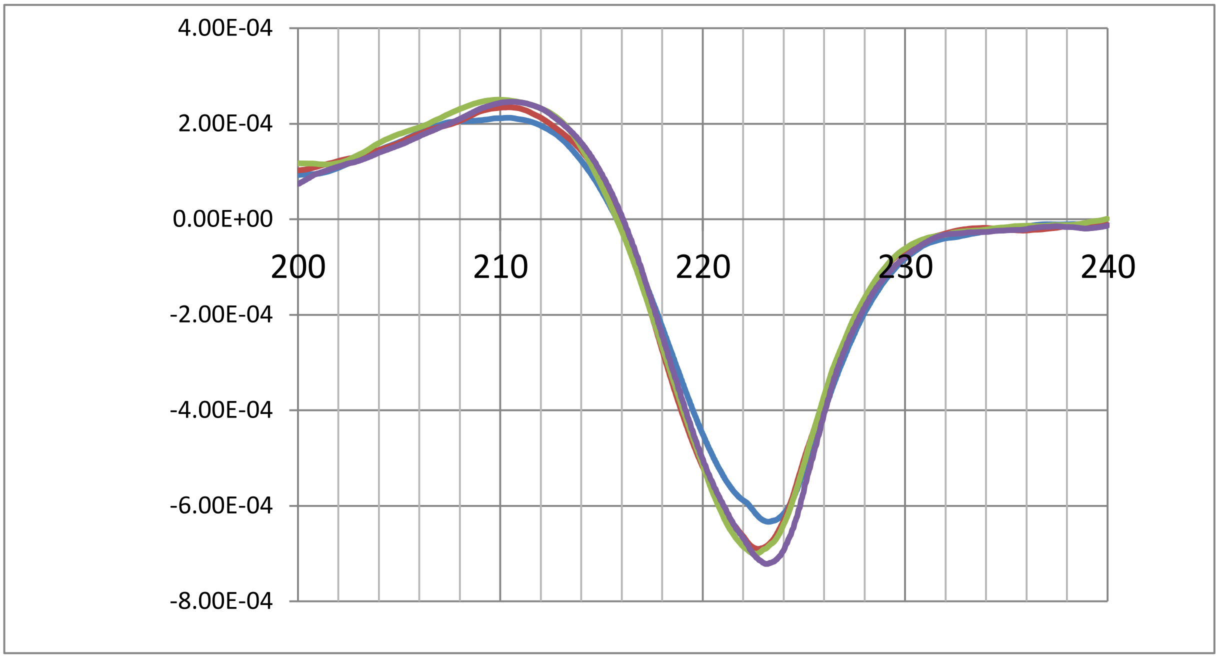


Figure 8 *TSSP peaks of sample 2*

Conclusion

- TA Instruments Q2000 DSC calorimeter is a very suitable instrument to apply DSC Method for Fuel Channel Hydrogen Equivalent Concentration Measurements.
- Reproducibility of the peak center is in the range of ±1 °C. Because the DSC method is a nondestructive method, the precision of measurements can be improved by increasing the number of measurements per sample.
- The shape of the samples has direct impact on the results. Due to this fact, for calibration purposes it is necessary to use either samples having the same shape as the ones to be measured or combination of samples (stacked, for examples) that, one in all, present the same dimensional characteristics as the sample to be measured.
- The DSC Method is able to measure hydrogen concentration for small samples having masses down to few milligrams.

References

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