# DETERMINATION OF HYDROGEN CONCENTRATION IN ZIRCONIUM ALLOYS BY DIFFERENTIAL SCANNING CALORIMETRY (DSC)

*M. MINCU, R. MARINESCU*
*Institute for Nuclear Research Pitesti,*
*Campului Str., Nr. 1, POB 78, 115400 - Mioveni, Arges, Romania*
*E-mail: marin.mincu@nuclear.ro*

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. 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.
This paper contains experimental work for hydrogen concentration determination by Differential Scanning Calorimetry (DSC) method. A study on the influence of sample mass and sample shape is presented. Also, the reproducibility and accuracy of the method used at INR Pitesti are presented.

**Key words: Differential Calorimetry, DSC, zirconium alloys**

## 1. Introduction

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. 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. The precipitation of zirconium hydride damages the mechanical properties.

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.

## 2. 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;
- 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.

Differential scanning calorimetry or DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature.

The basic principle underlying this technique is that when the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature. Whether less or more heat must flow to the sample depends on whether the process is exothermic or endothermic.

In order to determine the hydrogen concentration in zirconium alloys, the Differential Scanning Calorimetry method is used to measure the heat flow change during the hydrides dissolution on warm up and precipitation on cool down.

## 3. Experimental work

The DSC method was selected for this work because it is simple, relatively fast and gives good reproducibility. DSC is a nondestructive method, so repeat test runs on the same sample can be carried out. The technique is suitable to measure small samples and is used for material characterization of Zr-2.5Nb CANDU pressure tubes during the operation to assess its structural integrity and to predict its behavior until the next in-service inspection.

The DSC method is used to determine hydrogen dissolution and precipitation temperatures.
As is presented in [1], the terminal solid solubility of hydrogen in Zircaloy $C_H$ has previously been measured and is given by $C_H=A \exp(-E_H/T)$ where A is a constant, equal to $1.2x10^5$ wt. ppm, and $E_H$ is the difference in 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 have 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 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.

### 3.1. Sample analysis for calibration

Three samples of pressure tube (Zr-2.5Nb) with known hydrogen concentration were annealed in order to demonstrate the reproducibility and accuracy of the DSC method and also to calibrate the instrument. The measurements were made with samples encapsulated in aluminum pens and an empty pen was used as reference.

Sample 1 – Zr-2.5Nb, mass: 45 mg, hydrogen concentration: 30 ppm.

In Figures 1 and 2 are presented spectra obtained for two measurements repeated sequentially. We can see a very good shape of the peaks in the derivative heat flow. The peak center was taken for determination of hydrogen concentration. This represents the position of heat flow maximum slope.

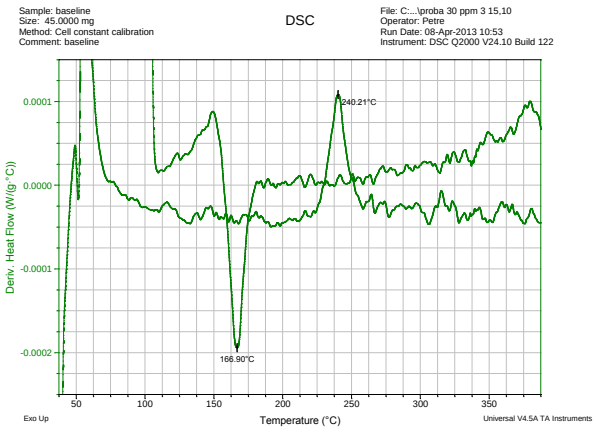


*Figure 1. – First measurement of sample 1*

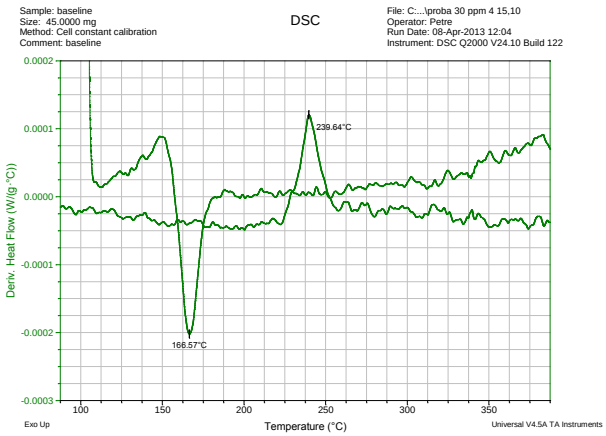


*Figure 2. – Second measurement of sample 1*

In figures 3 and 4 are presented in detail the TSSD and TSSP peaks for both measurements. We can see that the peak position is reproducible with a precision less than ±1°C.

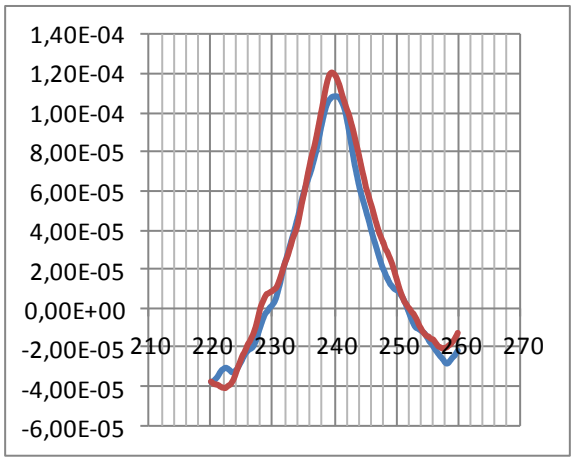


*Figure 3. – TSSD peaks of sample1*

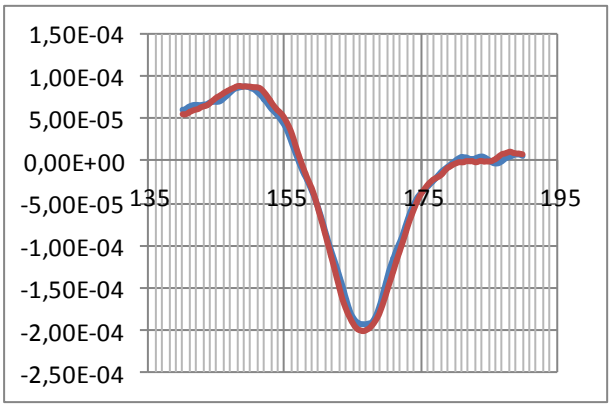


*Figure 4. – TSSP peaks of sample1*

Sample 2 – Zr-2.5Nb, mass: 28.13 mg, hydrogen concentration: 60 ppm.

In Figure 5 is presented spectrum obtained for sample 2. We can see higher peaks even though the sample mass is significantly less.

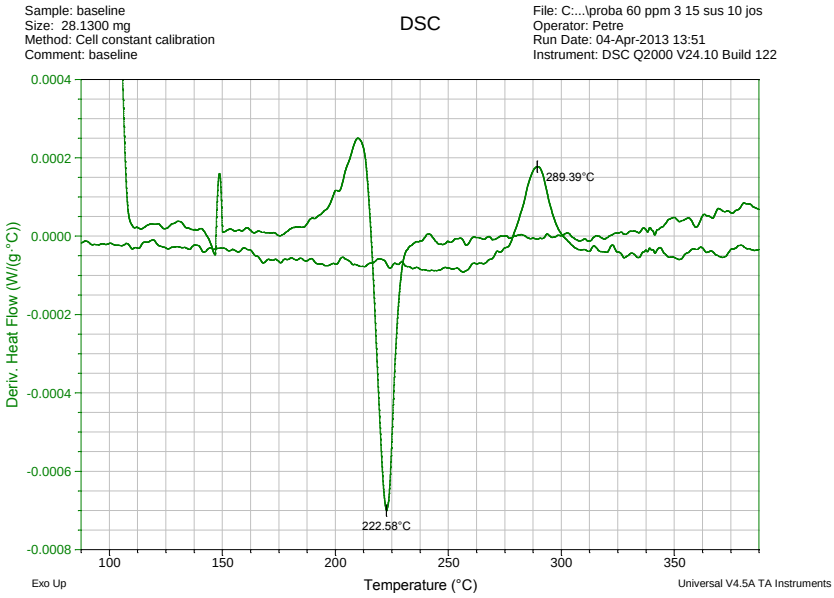


*Figure 5. – Deriv. Heat flow of sample 2*

In figures 6 and 7 are presented in detail the TSSD and TSSP peaks for four sequentially measurements. We can see that the peak position is also reproducible with a precision less than ±1°C.

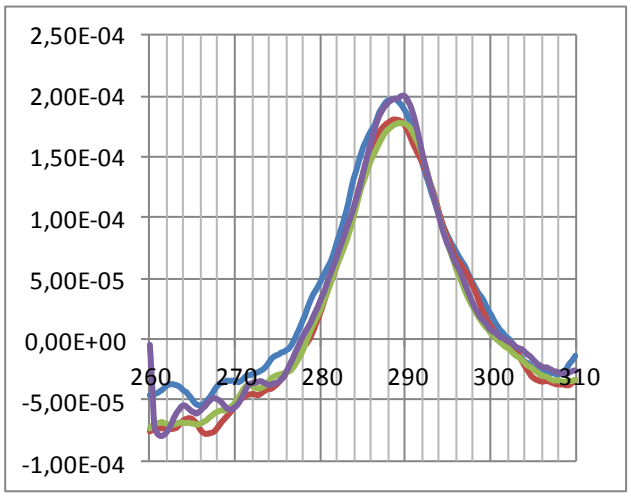


*Figure 6. – TSSD peaks of sample2*

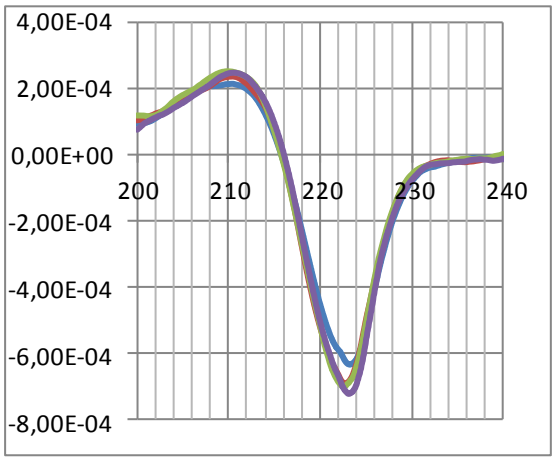


*Figure 7. – TSSP peaks of sample 2*

Sample 3 – Zr-2.5Nb, mass: 32.27 mg, hydrogen concentration: 100 ppm.

In Figure 8 is presented spectrum obtained for sample 3. As was expected, comparing with preview spectra we can see the peaks height increase with hydrogen concentration.

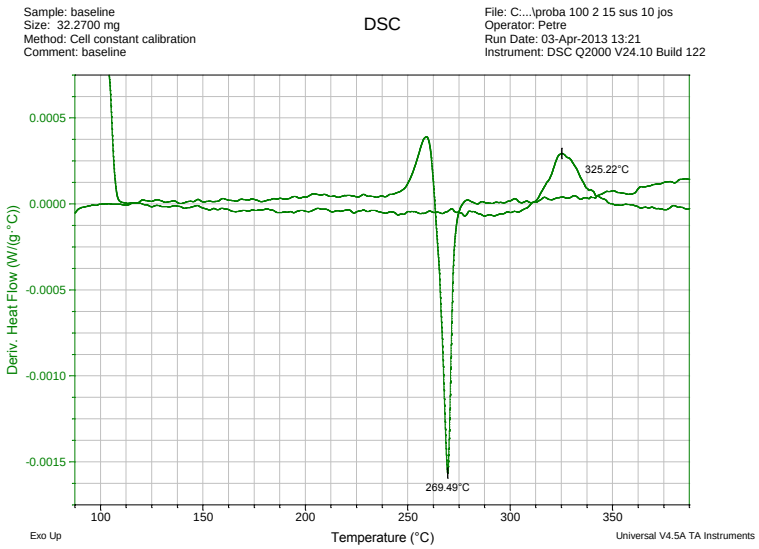


*Figure 8. – Deriv. Heat flow of sample 3*

In figures 9 and 10 are presented in detail the TSSD and TSSP peaks for three sequentially measurements. We can see that the peak position is also reproducible with a precision less than ±1°C.

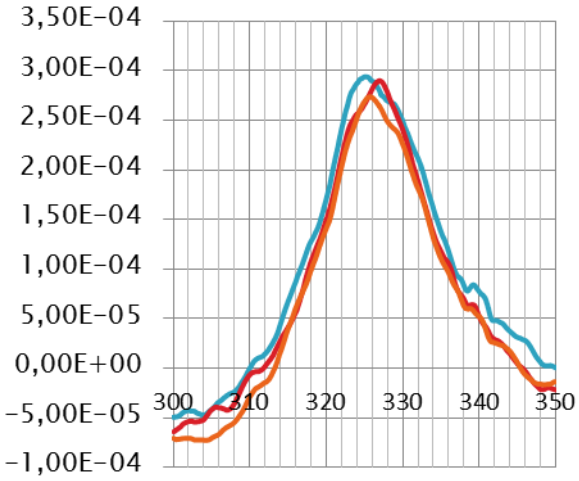


*Figure 9. – TSSD peaks of sample 3*

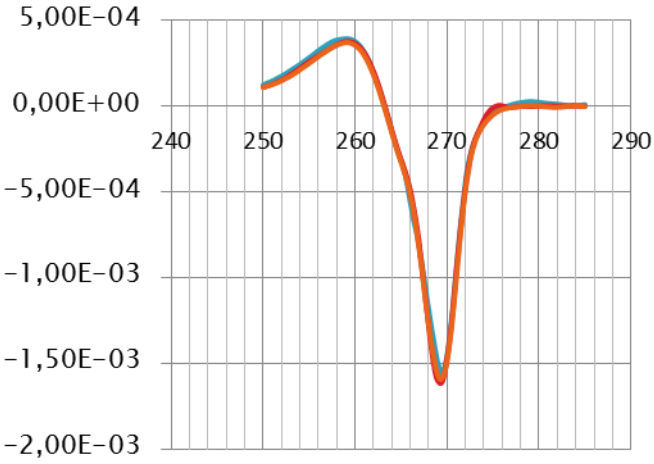


*Figure 10. – TSSP peaks of sample 3*

In the following table are presented the temperatures correspondent to dissolution peaks and precipitation peaks.

| | Sample 1(30 ppm) | |
|---|---|---|
| No. | $T_D$ (°C) | $T_P$ (°C) |
| 1 | 240.21 | 166.90 |
| 2 | 239.64 | 166.57 |
| | | |

| | Sample 2 (60 ppm) | |
|---|---|---|
| No. | $T_D$ (°C) | $T_P$ (°C) |
| 1 | 288.86 | 223.52 |
| 2 | 288.81 | 222.76 |
| 3 | 289.39 | 222.58 |
| 4 | 289.39 | 223.15 |
| | | |

| | Sample 3 (100 ppm) | |
|---|---|---|
| No. | $T_D$ (°C) | $T_P$ (°C) |
| 1 | 325.22 | 269.49 |
| 2 | 326.92 | 269.21 |
| 3 | 325.65 | 269.26 |
| | | |

Using the relation $\ln(C_H) = \ln(A) - B*(1/T)$ we can fit the experimental points like in Figure 11. Average values were used for each sample.

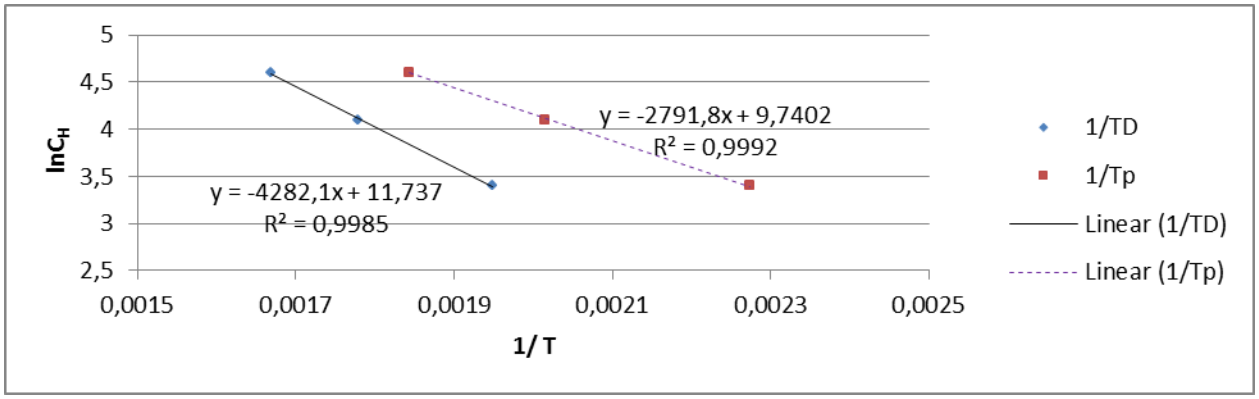


*Figure 11. Parameters obtained by linear fit*

Using the parameters obtained by fit we can write the relation for hydrogen concentration calculation.

$C_{TSSD}$= 125116*exp(- 35601/(RT)) and $C_{TSSP}$= 16987*exp(- 23211/(RT))

Where: R=8.314 J/K/mol and T temperature in K.

In the Figure 12 are shown the above equations together with other from references.

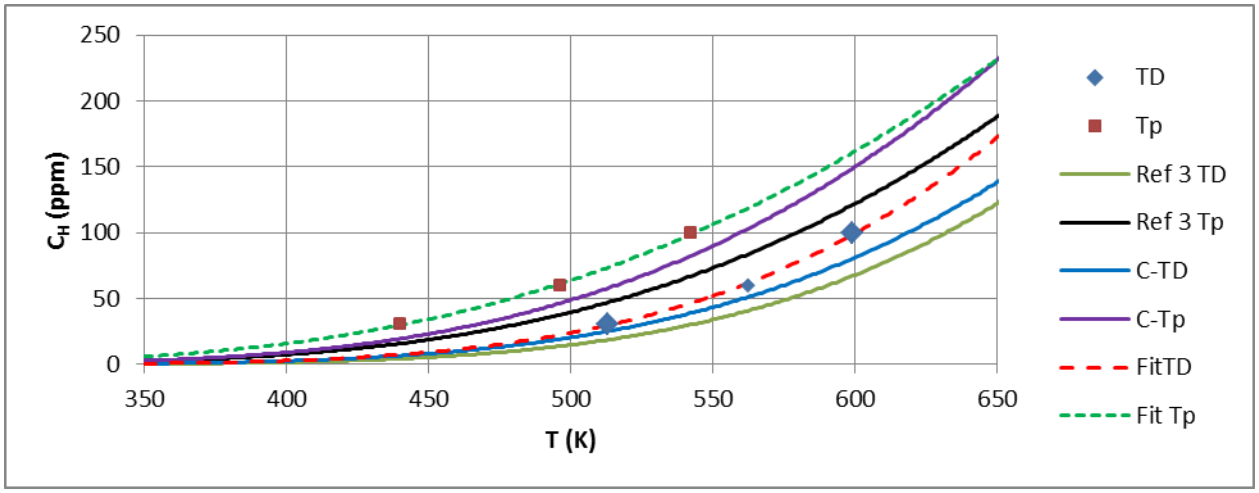


*Figure 12. Comparison between equations obtained in this work and other equations from references*

### 3.2. Influence of the sample preparation

Based on a significant number of experiments, there have been established the optimum working parameters to be used for measurements. These parameters are the pressure and flow of the inert gas, and increasing and decreasing temperature rate. It is also necessary to use temperature charts that assure the temperature stabilization.

In order to make a comparison of the results and to determine the influence of the preparation of the samples on the accuracy of the method, working parameters were kept unchanged throughout the analysis presented in the paper.

After cutting, the samples were washed in alcohol, and embedded in aluminum pans. The temperature increase rate was 15 °C/min and the cooling rate of 10 °C/min. There were analyzed samples with different concentrations: 25, 30, 60, 70 and 100 ppm hydrogen

respectively. The samples were cut into slices of 0.1 mm and 0.2 mm thickness and 0.5 mm thickness resulting into a parallelepiped shaped sample for the last one. The obtained foils were analyzed both individually and grouped - 2, 3, 4 of them or all 5 in the same pan.

We studied first of all the variation of the peaks form with concentration. In figure 13 we can see the dissolution peaks for five samples with hydrogen concentration ranging between 25 and 100 ppm.

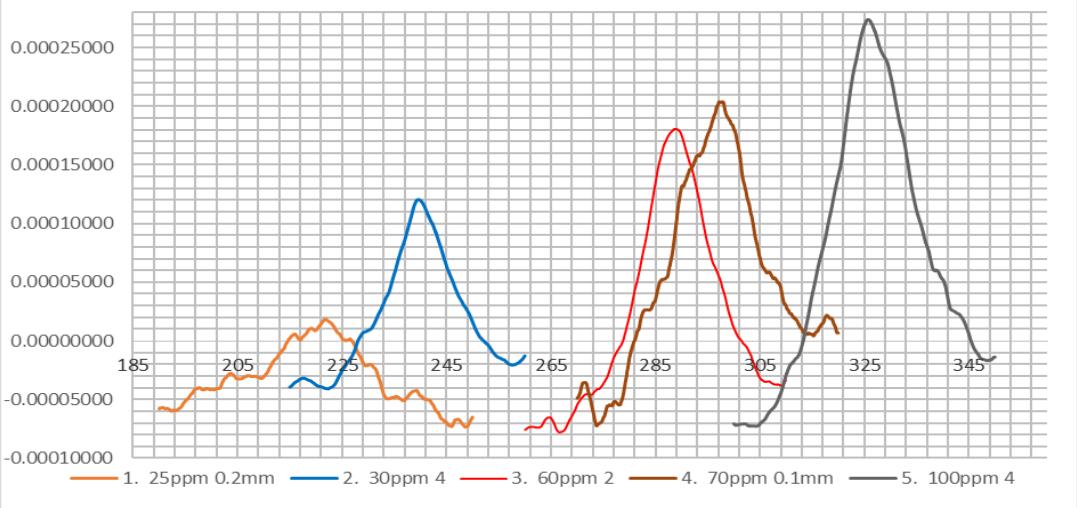


*Figure 13. TSSD peak for samples 1, 2, 3, 4, 5.*
*Sample 1: thin foil with hydrogen concentration of 25 ppm and 0.2 mm thick.*
*Sample 2: 30 ppm hydrogen and parallelepiped shape.*
*Sample 3: 60 ppm hydrogen and parallelepiped shape.*
*Sample 4: thin foil with hydrogen concentration of 70 ppm and 0.1 mm thick.*
*Sample 5: 100 ppm hydrogen and parallelepiped shape.*

It can be noted that when increasing the concentration of hydrogen, a movement of the dissolution peak position to higher temperatures and an increase in peak amplitude take place. For lower concentrations, the amplitude of the peaks decreases and, at the same time, the peaks lose their shape, being affected by noise.

In figure 14 are shown the peaks corresponding to the precipitation of hydrides for the five samples above described. We observe the same dependence, namely an increase in peak amplitude with increasing concentration. The accuracy of the method decreases for concentrations below 20 ppm.

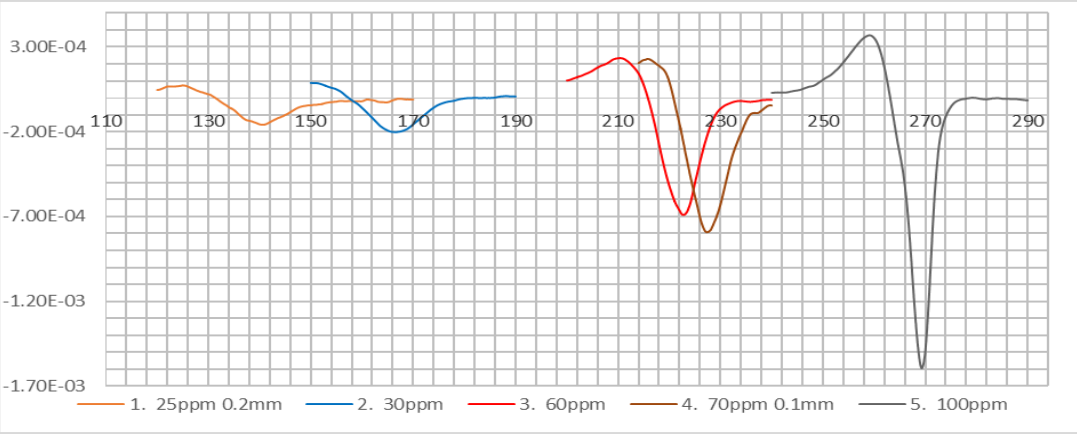


*Figure 14. TSSP peak for samples 1, 2, 3, 4, 5*

Another direction of this work was to test the influence of weight and shape of the sample on the results obtained. For this purpose, there were analyzed samples with the same hydrogen concentration, but with different masses and shapes. Figure 15 presents precipitation peaks for four samples with hydrogen concentration of 25 ppm having different masses and shapes.

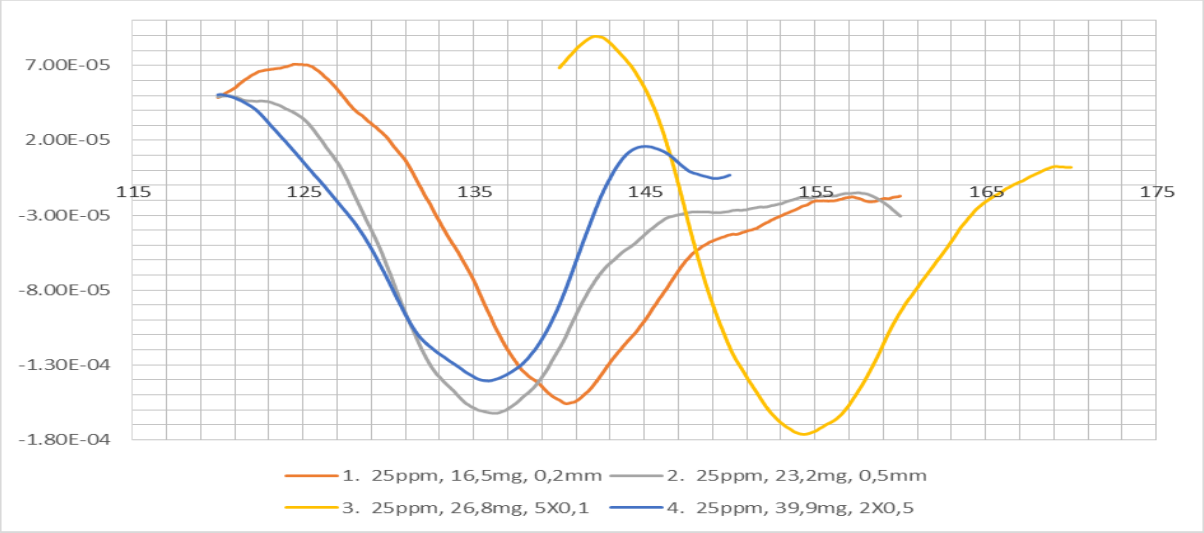


*Figure 15. Precipitation peaks for the 25 ppm hydrogen samples as follows*

Sample 1: thin foil weighing 16.5 mg and 0.2 mm thick.
Sample 2: parallelepiped sample weighing 23.3 mg and 0.5 mm thick
Sample 3: 5 stacked thin foils of 0.1 mm thickness each, with a total mass of 26.8 mg
Sample 4: 2 stacked rectangular samples 0.5 mm thick each, with a total mass of 39.9 mg

Comparing samples 2 and 4 of parallelepiped shape, it can be seen that there isn't an influence of mass on hydrogen concentration.
Comparing samples 2 and 3, of approximately equal masses, it is observed an influence of the shapes of the sample on the hydrogen concentration. It was observed that thin foils samples provide higher values of hydrogen concentration.
The same trend of dependence of the concentration on the shape of the sample is observed on the dissolution peaks shown in Figure 16. One observes that, although there is a quite big difference between the mass of the samples 2 and 4, the concentration of hydrogen is the same; in this case, the difference between the positions of the peaks is explained again by the shape of the samples.

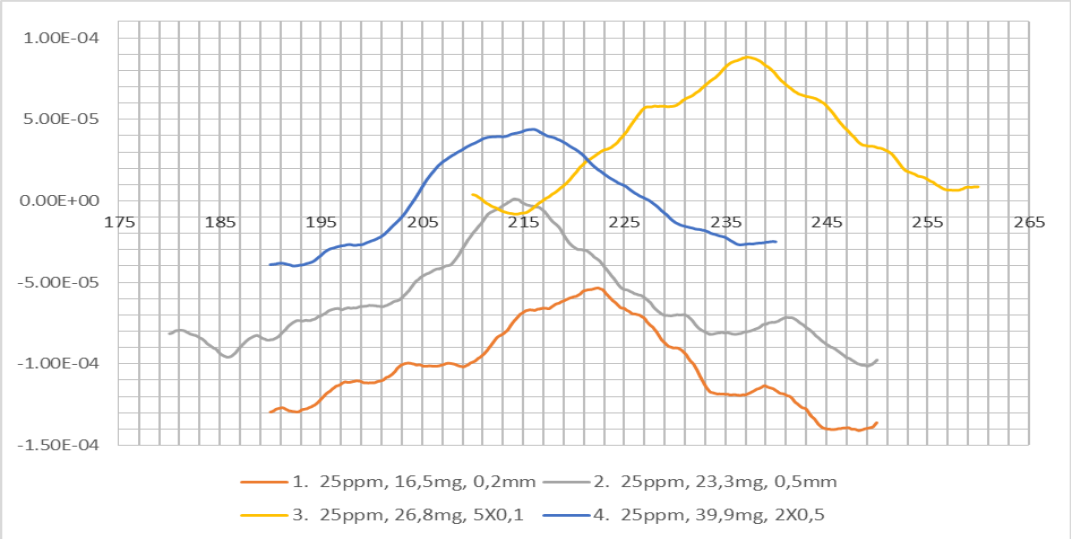


*Figure 16. Dissolution peaks for the 25 ppm hydrogen sample*

In order to check if this trend is still valid for higher concentrations, we analyzed a sample concentration of 70 ppm hydrogen. The results are shown in figure 17 and 18.

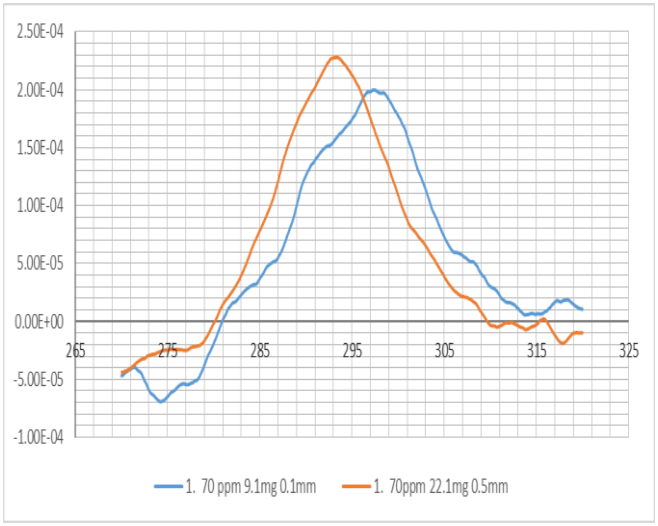


*Figure 17. Dissolution peaks for the 70 ppm hydrogen samples*

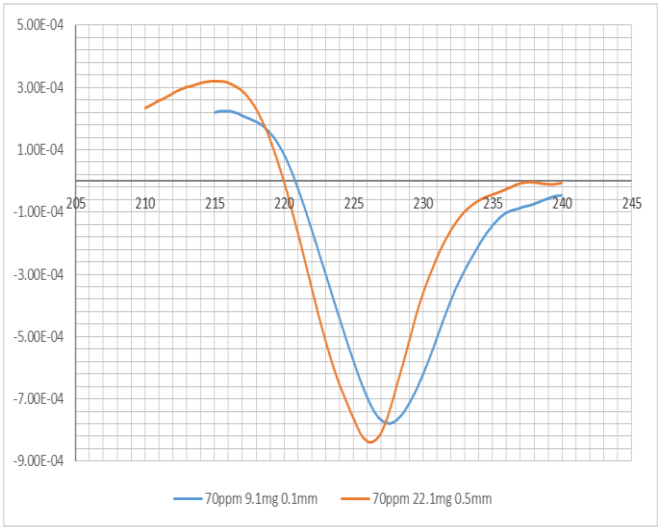


*Figure 18. Precipitation peaks for the 70ppm samples*

In Figures 17 and 18 the sample 1 is the thin foil of 0.1 mm thickness and mass of 9.1 mg and sample 2 is of parallelepiped shape with a thickness of 0.5 mm and weight of 22.1 mg.
As shown in Figures 15-18, the influence of sample shape on hydrogen concentration diminishes with increasing concentration.

## 4. Conclusions

- TA Instruments Q2000 DSC calorimeter is a 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 samples having the same shape as the ones to be measured.
- The DSC Method is able to measure hydrogen concentration for small samples having masses down to few milligrams.
- A good agreement was found between metallographic estimation of hydrogen concentration and DSC measurement for irradiated samples of Zy-4 cut from CANDU nuclear fuel sheath.

## 5. References

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