Specific heat of Zr-2.5Nb pressure tube material measured by differential scanning calorimetry (DSC)

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Abstract

Specific heats of Zr-2.5Nb pressure tube material have been measured by differential scanning calorimetry (DSC) between 100°C and 1200°C using a heating and cooling rate of 20°C/min. A hysteresis was observed in the specific heat curves between heating and cooling. A maximum value occurs at a higher temperature on heating than on cooling, and the magnitude is larger for cooling when compared to heating. The as-manufactured tube material showed a small enthalpy change during first heating, attributed to decomposition of meta-stable β-Zr; and this did not appear on second heating after being first heated to 1200°C. Further studies are suggested to characterize the hysteresis behaviour.

1. Introduction

Zr-2.5Nb alloy is used for the pressure tubes in CANDU®[1] reactor fuel channels. The pressure tubes are fabricated by hot extrusion of hollow billets into tubes, which are then cold-drawn (25-30%) and stress relieved for 24 hr at 400°C in a steam-autoclave [1]. The resulting microstructure of the pressure tube consists of elongated hexagonal close-packed (hcp) α-Zr grains containing a high dislocation density, and a thin layer of body-centered cubic (bcc) β phase at the α-grain boundaries (Figure 1). Small quantities of meta-stable ω phase may also exist in the material, depending on the thermo-mechanical history. At room temperature, a typical pressure tube contains mostly α-phase Zr with ≈1wt% Nb and a small amount of Nb-stabilized β phase with ≈20wt% Nb from the autoclaving treatment.

In reactor, the pressure tube normally operates at ≈300°C. In the event of a hypothetical loss-of-coolant accident, the pressure tube may be subjected to a high temperature transient up to 1200°C, resulting in α→β phase transformation, Figure 2 [2]. The phase transformation changes the proportions of the α- and β-phase material and the evolution of α-Zr texture during heating has been previously found to be stable [3]. These metallurgical changes (from hcp→bcc and their compositions) can affect the mechanical deformation behavior of the pressure tube material. Other behaviors such as the thermal expansion characteristics of

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[1] CANDU® (CANada Deuterium Uranium) is a registered trademark of Atomic Energy of Canada Limited.

CANDU pressure tube material have also been found to be dependent on its crystallographic texture and phase transformation [4].

The thermal properties such as the enthalpy and specific heat capacity of the pressure tube material are also affected by the phase changes. Therefore, it is important to know the thermal properties for Zr-2.5Nb pressure tube material, in order to predict the tube's performance under extreme thermal transient conditions. Some specific heat data over a high temperature range on Zr-2.5Nb alloy wire, obtained using an adiabatic calorimeter, are reported in the literature [5]. However, the material's metallurgical condition in this alloy investigated [5] is not representative of that in a typical CANDU Zr-2.5Nb pressure tube material. Although there is also some limited low-temperature data up to 400°C available on Zr-2.5Nb pressure tube material [6], such data is not easily extended to higher temperatures relevant to accident conditions.

This study investigated the specific heat capacity of an as-manufactured Zr-2.5Nb pressure tube material using differential scanning calorimetry (DSC) from 100°C to 1200°C. The effects of thermal cycles were evaluated with a same heating and cooling rate of 20°C/min. This paper summarizes the results with a comparison with literature, and provides some explanation for the different characteristics and behavior in specific heat that are observed in this study.

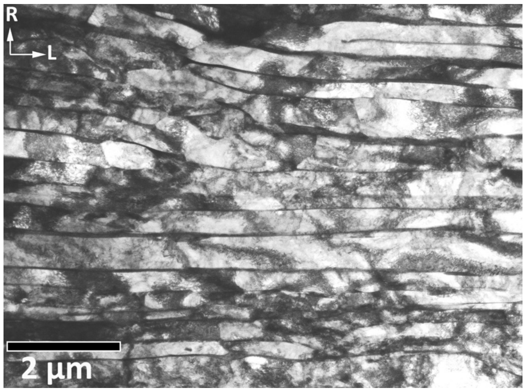


Figure 1 A transmission electron micrograph of as-received Zr-2.5Nb pressure tube showing elongated α-Zr grains containing a high density of dislocations and a thin layer of β–phase at the α–grain boundaries. The labels R and L denote radial and longitudinal directions of the tube, respectively.

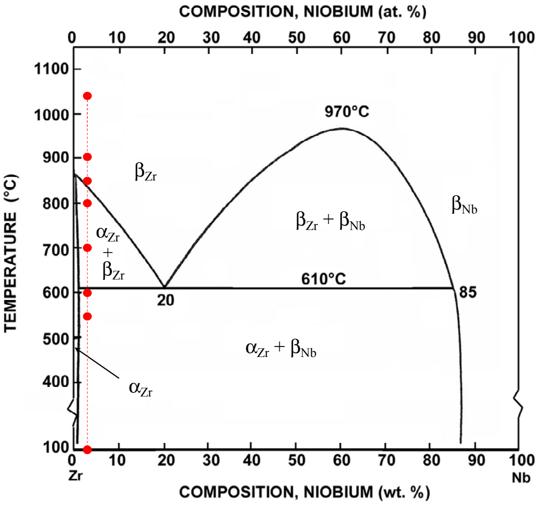


Figure 2 Zr-Nb phase diagram [2]. The vertical dashed line in the phase diagram corresponds to the Zr-2.5Nb composition. (The points along the composition line indicates the temperatures used in a previous neutron diffraction study [3]).

2. Experimental

2.1 Specimen preparation

Solid rods, about 4 mm in diameter, were machined from the longitudinal direction of an as-manufactured Zr-2.5Nb pressure tube. The rods were then sliced into 1-mm thick flat discs using a slow-speed diamond saw. The flat surfaces were slightly polished to provide a good contact, and a maximum surface area, between the disc and the specimen crucible that is used in the DSC measurements. The disc specimens were ultrasonically cleaned with acetone before they were used for testing.

2.2 Differential scanning calorimetry (DSC) method for specific heat measurements

In the DSC method, two identical pans (one for the sample crucible and an empty crucible for reference) are instrumented with thermocouples beneath the pans. The two pans are heated and cooled by controlling the furnace temperature under a heat flux control. The specific heat values of the sample are obtained using a ratio method with a standard material (e.g., sapphire) with well known specific heat. The difference in temperature between the sample pan and the other (empty) pan is measured as a function of temperature.

In this study, the specific heat (C_p) values of Zr-2.5Nb pressure tube samples were measured using a NETZSCH DSC STA 449C Jupiter thermal analyzer (Figure 3a). The instrument has a specified DSC resolution of < 1 μW. The thermal analyzer used for the C_p measurements consists of these basic elements:

(i) a sample carrier for the DSC-based C_p measurements
(ii) a furnace (rhodium)
(iii) Type S thermocouple
(iv) Purging with high purity argon gas (50 ml/min)
(v) Calibration standard sapphire disc
(vi) Pt-Rh crucibles with pierced lids and Y_2O_3 liners
(vii) Oxygen Trap System (OTS STA) installed to remove traces of oxygen out of the purge gas.

For the C_p measurements obtained in this study, the oxygen trap system was used while measuring the specific heat of Zr-2.5Nb pressure tube samples since zirconium oxidizes readily when heated to high temperatures.

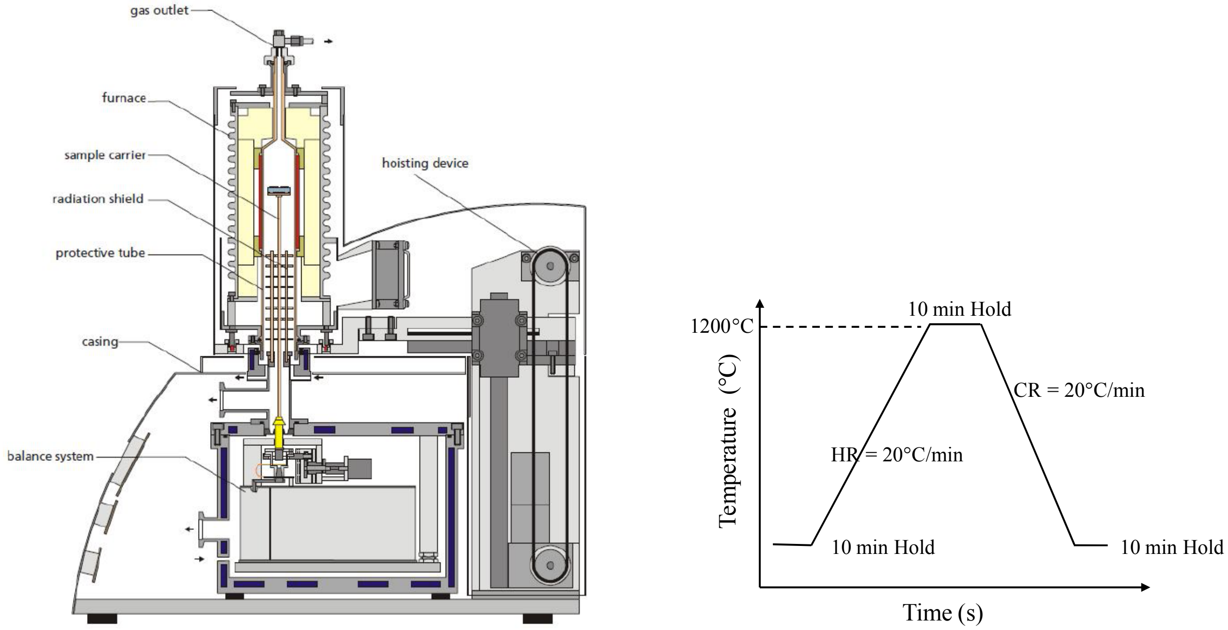
The specific heat of a sample is obtained by a ratio method, using Equation (1),

$$C_{p\,(sample)} = \frac{m_{standard}}{m_{sample}} \times \frac{DSC_{sample} - DSC_{baseline}}{DSC_{standard} - DSC_{baseline}} \times C_{p\,(standard)} \qquad (1)$$

where $C_{p\text{ (sample)}}$ is the specific heat of the sample at temperature T, $C_{p\text{ (standard)}}$ is the known standard specific heat of standard (sapphire) at temperature T, m_{standard} and m_{sample} are the masses of the sapphire and sample, respectively, and DSC_{sample}, DSC_{standard}, and DSC_{baseline} are the values for the heat flux signal at temperature T.

Three separate measurements are required to obtain the specific heat of the sample. A baseline measurement is performed using the heat flux based DSC on an empty sample crucible and a reference crucible made of Pt-Rh. Another measurement is made using a sapphire standard sample placed in the sample crucible. Once these two measurements are obtained (baseline with empty and reference crucibles and sapphire standard), the test samples can be conducted with the sample now placed in the sample crucible to obtain the DSC curve. From Equation (1), the specific heat of the sample is obtained as a function of temperature.

In this study, the specific heats of triplicate disc specimens of as-manufactured Zr-2.5Nb pressure tube material were measured by heating from 100°C to 1200°C with a 20°C/min heating rate, isothermally holding for 10 min and cooling down to 100°C with a 20°C/min cooling rate (Figure 3b). To evaluate the effect of thermal cycling, the same samples were given a second same thermal cycle. NETZSCH Software was used to control the thermal cycle and to evaluate the DSC data obtained to determine the specific heat values based on Equation (1).



(a) (b)

Figure 3 (a) Schematic diagram of a NETZSCH DSC thermal analyzer. (b) Temperature versus time cycle used in DSC Cp measurements performed in this study.

3. Results and Discussion

3.1 DSC C_p curves from 1st thermal cycle (Run 1)

The specific heat (C_p) curves during heating and cooling for the 1st thermal cycle are given in Figure 4. Figure 4a gives the C_p curves for the heat-up part of the cycle. The cool-down portion is given in Figure 4b.

Examination of Figure 4a indicates that there are 3 enthalpy peaks during heating of samples of as-manufactured Zr-2.5Nb pressure tube. From the triplicate samples tested, the data scattering for heating is estimated to be about 10%. The two smaller enthalpy peaks (#1 and #2) are located at 500°C and 615°C. The largest enthalpy peak (#3) is located at around 810°C. These 3 enthalpy peaks which occur during heating are endothermic reactions as previously observed in DSC heat flow analysis of Zr-2.5Nb pressure tube material [7].

The smallest enthalpy peak (#1) is attributed to a further decomposition of the meta-stable β-Zr that is previously present in the pressure tube material from the stress-relief autoclaving treatment. The decomposition of meta-stable β_{Zr} into the stable β_{Nb} phase occurs via the following reactions [8].

$$\beta_{Zr} \rightarrow \omega + \beta_{enr} \tag{2}$$
$$\beta_{enr} \rightarrow \omega + \beta_{Nb} \tag{3}$$
$$\omega \rightarrow \alpha_{Zr} + \beta_{Nb} \tag{4}$$

combining Equations 2, 3 and 4 gives,

$$\beta_{Zr} \rightarrow \alpha_{Zr} + \beta_{Nb} \tag{5}$$

β_{enr} is enriched in niobium, and ω is a meta-stable hexagonal close-packed phase. Under practical terms, the stable β_{Nb} phase may not be achieved since the temperature-time-transformation (TTT) diagram developed for the β-phase in Zr-2.5Nb pressure tube material indicates that the meta-stable β_{Zr} is most likely to transform into a β_{enr} phase [9]. In considering the above decomposition reactions, it is likely that the occurrence of enthalpy peak #1 is attributed to a combination of reactions in Equations (3) and (4).

The occurrence of enthalpy peak #2 at 610°C can be attributed to changes in α-Zr grain shape from elongated to equiaxed with some grain growth and an initiation of phase transformation in converting the α_{Zr} and ω material into β_{Zr}. In addition, some re-distribution of niobium in decomposed product of β_{Nb} (≈20wt% Nb) into β_{Zr} (diluted in Nb content) may also contribute to the enthalpy increase at this higher temperature of 610°C.

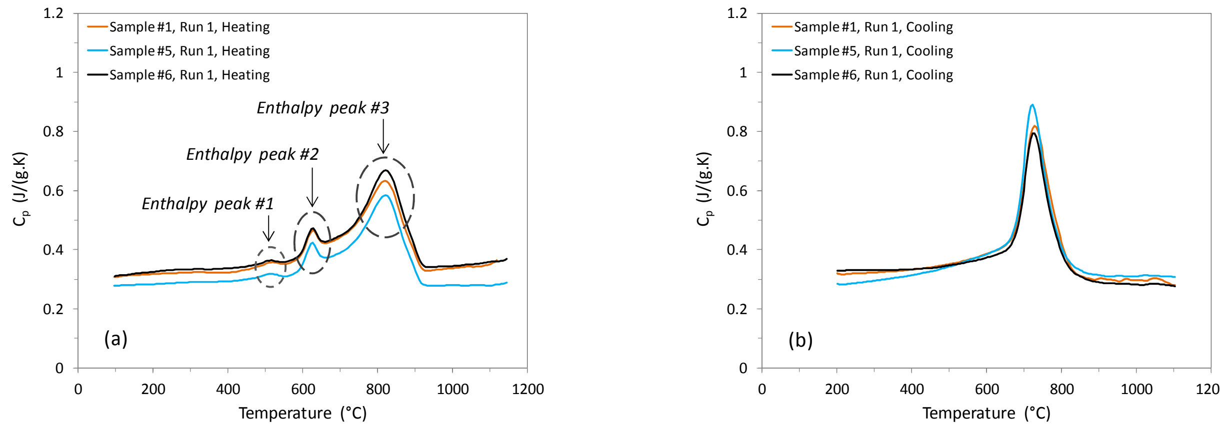


Figure 4 C_p results from triplicate samples for 1st thermal cycle: (a) heating, and (b) cooling.

Examination of Figure 4b (cool-down part of the 1st thermal cycle), indicates that there is only one enthalpy peak located at about 720°C. The data scattering estimated for cooling from the triplicate samples tested is about 10%. The enthalpy peak observed during cooling has been previously determined by DSC heat flow analysis on Zr-2.5Nb pressure tube material to be an exothermic reaction [7].

In comparing the C_p peak temperatures between heating (for the largest enthalpy peak) and cooling (Figure 4), there is a hysteresis observed where the $C_{p\ (heating)}$ peak temperature (810°C) is higher than the $C_{p\ (cooling)}$ peak temperature (720°C). The reason for this hysteresis is not clearly known at this time. On cooling from 1200°C to 100°C, a reverse transformation of $\beta \rightarrow \alpha$ occurs in the sample as the cooling of the material traverse across the $(\alpha+\beta)/\beta$ transus and $\alpha/(\alpha+\beta)$ boundary. Further experiments are suggested to help resolve this difference in behavior between heating and cooling responses using multiple heating-cooling schedules between the temperature range of 600 to 950°C, the $(\alpha+\beta)$ domain, to characterize the underlying mechanisms of the hysteresis behavior.

3.2 DSC C_p curves from same samples in the 2nd thermal cycle (Run 2)

From the 2nd thermal cycle tested on the same triplicate samples, the C_p curves obtained for heating and cooling are shown in Figure 5. The data scattering for heating is estimated to be about 10%, similar to that produced from the 1st thermal cycle. The data scattering for cooling is about 30%, which much larger than that of heating. There are also some variations in the overall slopes of the C_p curves, with a larger spread shown by the cooling slopes.

In Figure 5a, there is only one enthalpy peak observed during the 2nd heating, after the same sample had been first heated at 1200°C. At temperatures below 300°C and above 950°C, the individual C_p curves showed some variations which are likely due to noise in the data. Although there is a small peak at about 280°C which may be attributed to hydride dissolution on heating (Figure 5a), this peak should also appear but is absent during the 1st heating cycle (Figure 4a). The reason for this is not known. At about 1000°C, the reason is also not known for the inconsistent variations in the Cp curves between the three samples. The C_p peak temperature during heating is located at about 810°C (Figure 5a), the same temperature as that seen in the 1st heating (Figure 4a). The enthalpy peak in the 2nd heating is also an endothermic reaction. This enthalpy peak is solely a direct result of the phase transformation of $\alpha \rightarrow \beta$.

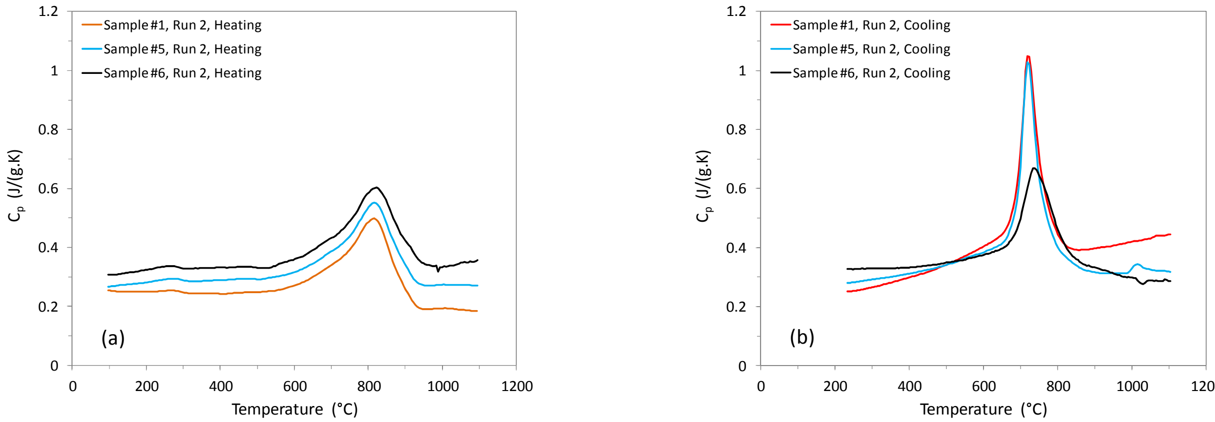


Figure 5 C_p results from the same samples for the 2nd run on: (a) heating, and (b) cooling.

3.3 Comparison of averaged C_p curves (from triplicate samples) and enthalpy

Figure 6 shows a further comparison of an averaged C_p curve for heating and cooling between the 1st and 2nd thermal cycle. As can be seen in the figure, the two smaller peaks from the 1st thermal cycle (shown by the red dashed line) are absent during the heating in the 2nd thermal cycle. The maximum C_p value during cooling is about 30% larger than that during heating, and the $C_{p\ (cooling)}$ peak is narrower than the $C_{p\ (heating)}$ peak. The averaged $C_{p\ (heating)}$ curve from this study has a very small slope (as indicated by the grey dashed line).

Using the averaged C_p curves, the estimated specific enthalpy values are given in Table 1. The enthalpy during the 1st heating is slightly larger than that in the 2nd heating. This difference has been attributed to the compositional changes in the partially decomposed β-phase material.

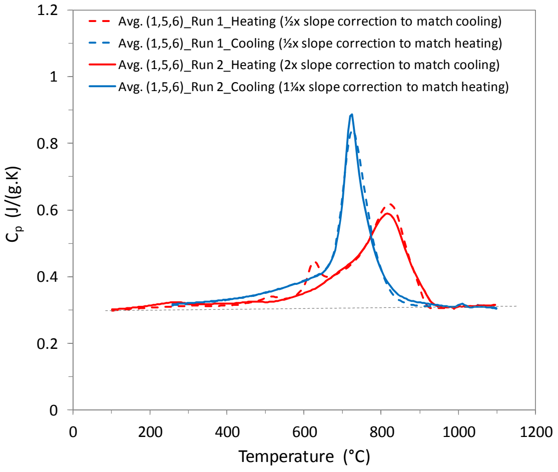


Figure 6 C_p results from 1st run and 2nd run on the same samples during heating and cooling.

Table 1 Enthalpy estimated using integrated area under the C_p curve from 400°C to 1000°C

Thermal Cycle	Specific Enthalpy (J/g)		% Difference: (Run 1 – Run 2) ÷ (Run 1)
	Run 1	Run 2	
Heating	11.222	10.511	6.77
Cooling	13.425	13.422	-0.02

3.4 Comparison of averaged C_p curves with literature and β phase fraction

Figure 7 shows a comparison between the averaged C_p curves for the 1st and 2nd thermal cycle from this study and the earlier work by Roshchupkin et al. [5]. For evaluation, Figure 7a and 7b include the evolution of β-phase fraction in Zr-2.5Nb pressure tube material with temperature changes during heating and cooling, previously measured by neutron diffraction [3].

In Figure 7 (1st thermal cycle), the averaged $C_{p\text{ (heating)}}$ curve shows some agreement with Roshchupkin et al. data [5] from about 400°C to 800°C. The two $C_{p\text{ (heating)}}$ peak temperatures and maximum values appear to be in good agreement. The two C_p peaks occur at a temperature corresponding to about 50% β-phase present in the alloy from the phase transformation of $\alpha \rightarrow \beta$ which occurs during heating. At the low temperature end, the Roshchupkin et al. C_p values showed a large scatter, where this data scattering may be due to decomposition of the meta-stable β-phase material that was also observed in this study when an autoclaved Zr-2.5Nb pressure tube material was given a 1st heating to high temperatures.

Also seen in Figure 7, the Roshchupkin et al. C_p values started to remain constant as the material was heated from 850°C to 900°C. It could be assumed that the $(\alpha+\beta)/\beta$ transus for that material is at 850°C. In this study, the $(\alpha+\beta)/\beta$ transition temperature is located at about 910°C [6]. The $(\alpha+\beta)/\beta$ transus is known to be affected by interstitial solutes in Zr-based alloy systems. Oxygen is a strong α-phase stabilizer, and Nb and Fe stabilize the β-phase. The chemical composition specification of the ingot used to manufacture this pressure tube material that is used in this study is 2.52-2.57 wt% Nb, 1190-1220 ppm O, 350-410 ppm Fe and the balance is Zr. In Roshchupkin et al. [5] experiments, there is no indication for oxygen concentration in the Zr-2.5Nb alloy material that was used in their C_p measurements. With a lower (C_p) transition temperature, the oxygen level was likely much lower than 1190 ppm in the Roshchupkin samples.

For cooling, there are no literature data for comparison. As discussed earlier, a further study into this hysteresis behaviour is suggested, including much faster rates of heating and cooling to investigate non-equilibrium behaviour of specific heat.

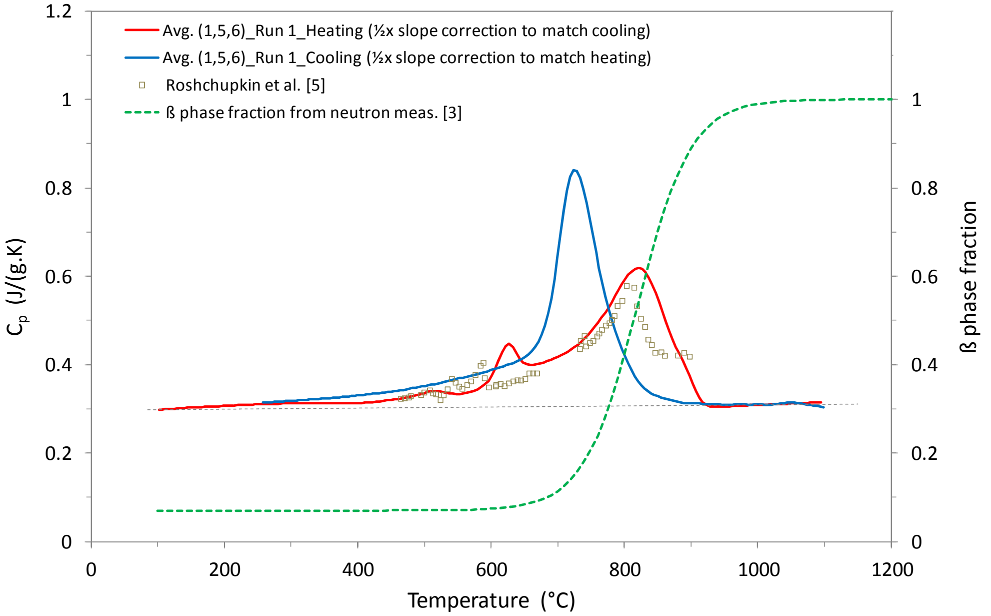


Figure 7 Comparison of averaged C_p results from triplicate samples with slope corrections for the 1st thermal cycle with Roshchupkin et al. and previous β-phase fraction data obtained from neutron diffraction study [3].

4. Concluding Remarks

The specific heat (C_p) of triplicate disc samples taken from an as-manufactured Zr-2.5Nb pressure tube has been measured using the differential scanning calorimetry (DSC) method for two thermal cycles from 100°C to 1200°C with the same rate of heating and cooling. The following conclusions can be drawn from this study.

1. The samples of as-manufactured pressure tube when heated during the 1st thermal cycle gave 3 distinct enthalpy peaks which are all endothermic reactions. The 1st enthalpy peak (smallest) is located at 500°C and is attributed to a further decomposition of meta-stable β-phase material that was previously produced from the autoclaving treatment of the pressure tube. The 2nd enthalpy peak (somewhat larger than the 1st peak) is located at 615°C, this enthalpy increase has been attributed to mixed microstructural changes (e.g., a grain shape change and growth combined with a precursory initiation of phase transformation of α→β, and possibly with some re-distribution of niobium in the Zr lattice at these higher temperatures. The 3rd enthalpy peak (largest) is located at 810°C, corresponding to about 50% β-phase material in the sample, is primarily due to the full phase transformation of α→β.

2. On cooling from 1200°C, the samples gave one enthalpy peak which is an exothermic reaction located at 720°C, suggesting that there is a hysteresis behavior in the C_p curves during heating and cooling.

3. When a 2nd thermal cycle was applied to the same samples previously tested in the 1st thermal cycle, these (high-temperature annealed) samples produced only one endothermic enthalpy peak during heating and one exothermic enthalpy peak on cooling. The locations of these peaks are at the same temperatures as those seen in the 1st thermal cycle, with the heating enthalpy peak corresponding to about 50% β-phase in the material.

4. The specific heat (C_p) curves averaged from these triplicate samples gave a good agreement with literature (Roshchupkin et al.) data up to the maximum C_p value [5]. The agreement is poor beyond the C_p peak temperatures, which could be expected since the condition of the Zr-2.5Nb wire material tested by Roshchupkin et al. is likely not similar to or representative of the CANDU Zr-2.5Nb pressure tube material used in this study.

5. References

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