



DSC “peak temperature” versus “maximum slope temperature” in determining TSSD temperature

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ABSTRACT

One of the concerns of the nuclear industry is the deleterious effect of hydrogen on the structural integrity of the reactor core components due to delayed hydride cracking (DHC). The DHC process occurs when hydrogen concentration exceeds the terminal solid solubility (TSS) in the component. Thus, the accurate knowledge of TSS is necessary to predict the lifetime of the components. Differential scanning calorimetry (DSC) is normally used to measure the hydrogen TSS in zirconium alloys. There is a measurable change in the amount of heat absorbed by the specimen when the hydrides dissolve. The hydride dissolution process does not exhibit a well-defined “sharp” change in the heat-flow signal at the transition temperature. A typical DSC heat-flow curve for hydride dissolution has three definite features; “peak temperature” (PT), “maximum slope temperature” (MST) and “completion temperature”. The present investigation aims to identify the part of the heat-flow signal that closely corresponds to the TSS temperature for hydride dissolution (T_{TSSD}).

Coupons were cut from a Zr–2.5Nb specimen, which had been previously hydrided using an electrolytic cell to create a surface hydride layer of $\sim 20 \mu\text{m}$ thick on all sides of the specimen. The coupons were then annealed isothermally at various temperatures to establish the T_{TSSD} under equilibrium conditions. Subsequently the hydride layer was removed and the coupons were analyzed for TSSD temperature using DSC. The PT and MST for each DSC run were determined and compared to the annealing temperature of the coupon. The results show that the annealing temperature (the equilibrium T_{TSSD}) is much closer to the DSC PT than any other feature of the heat-flow curve.

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1. Introduction

Due to low neutron absorption cross section of Zr, Zr-based alloys such as Zircaloy-2, Zircaloy-4 and Zr–Nb alloys are used for manufacturing reactor core components. However, the terminal solid solubility (TSS) for H in Zr [1,2] is very low and the components can become susceptible to a process called “delayed hydride cracking” (DHC¹) if H concentration exceeds the TSS [3]. For example in Zr–2.5Nb (Zr–2.5 wt.% Nb), a two phase alloy used for pressure tubes in CANDU^{®2} power reactors, the TSS is about 70 mg/kg H at 300 °C [4]. Thus, the accurate knowledge of TSS is necessary to predict the lifetime of the components.

Differential scanning calorimetry (DSC) is usually used to measure the hydrogen TSS in zirconium alloys. Similar to melting,

hydride dissolution in alloys is an endothermic process [5]. There is a measurable change in the amount of heat absorbed by the specimen when the hydrides dissolve. Hydride dissolution process does not exhibit a well-defined “sharp” change in the heat-flow signal at the transition temperature. A typical DSC heat-flow curve for hydride dissolution is shown in Fig. 1 where three definite features are marked on; “peak temperature” (PT), “maximum slope temperature” (MST) and “completion temperature” (CT). Usually, the MST, being about the average of the three temperatures, is taken as the hydride dissolution temperature [6]. The present investigation aims to identify the part of the heat-flow signal that closely corresponds to the hydride dissolution temperature (T_{TSSD}).

In a set of TSS studies the solubility limit for hydrogen in pure Zr was examined using DSC [7]. As stated above, MST was initially taken as the T_{TSSD} . The results of such analysis reproduced in Fig. 2a to elucidate the point of discussion. In the figure, the dashed line represents the best fit to the pure Zr data [7] and the solid line represents the results obtained by Kearns for unalloyed zirconium [2]. Fig. 2a shows that there is a large difference between the pure Zr data obtained using DSC and Kearns' TSS line. One may argue that Kearns' line is the result of less accurate techniques used about four decades ago. On the other hand, it is also possible that the discrepancy arises from the misinterpretation of the DSC heat-flow

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¹ The time-dependent cracking involving hydrogen is called delayed hydride cracking or DHC. The DHC process involves diffusion of hydrogen to the flaw tip, followed by nucleation, growth, and fracture of the flaw-tip hydride. The process repeats and the crack propagates through the component at a rate that is mainly dependent on temperature.

² CANDU – CANada Deuterium Uranium is a registered trademark of Atomic Energy of Canada Ltd.

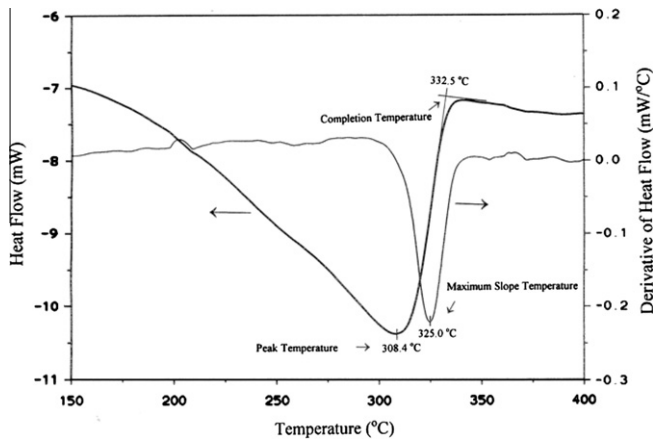


Fig. 1. DSC data from an α -Zr specimen containing 63 ± 3 mg/kg hydrogen obtained during heating. The plot shows the basic heat-flow response and its temperature derivative.

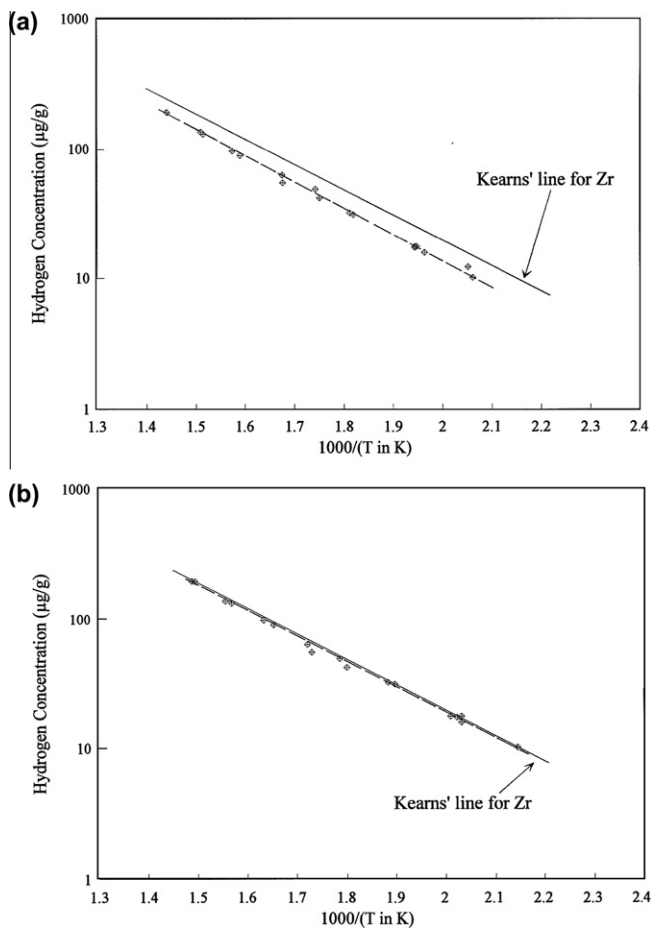


Fig. 2. TSSD for hydrogen in α -Zr (after [7]). The results were obtained by assuming: (a) MST (see the text and Fig. 1) and (b) PT as the TSSD temperature. The dashed lines are the best fits to the data. Kearns' line for unalloyed Zr [2] is included for comparison.

signal or from errors in the hydrogen concentration measurements. In Fig. 2b the same data as in Fig. 2a are presented again, except that this time peak temperature (as shown in Fig. 1) has been assumed to be the T_{TSSD} . In this case, as Fig. 2b shows, the results are very close to the Kearns' TSS line for unalloyed Zr and the discrepancy has disappeared. This indicated that the DSC peak temperature, rather than the maximum slope temperature, may be the right TSSD temperature. Motivated by these results, a set of

coordinated DSC and neutron diffraction (ND) measurements were carried out to remove the uncertainty and identify the part of the heat-flow signal that actually correspond to the hydride dissolution temperature [8]. The ND measurements showed that for both α - and β -Zr (Zr–20 wt.% Nb) the deuteride (the specimens were charged with deuterium instead of hydrogen in this specific cases) dissolution temperature correlates with the DSC PT.

In a recent paper Giroldi et al. [9] compared the results of their DSC and differential dilatometry (DD) measurements and also compared them with the results reported in the literature. They showed that their DD TSSD line is very close to their DSC PT line (Fig. 9 of [9]) as well as the Khatamian [4] TSSD line obtained using the DSC peak temperature (Fig. 14 of [9]), consistent with results from the neutron diffraction measurements [8]. However, they maintained that DD is less accurate than DSC and reported that the uncertainty in the DD and DSC measurements were evaluated to be about 5 °C and 2 °C, respectively. Thus, they argued that the uncertainty in the DD results may make their comparison with the results of other techniques less valid. In addition, Giroldi et al. discussed the coordinated DSC and ND results mentioned above [8] and the internal friction (IF) results of Pan and Puls [10], which they stated that have been interpreted to agree with the DSC MST. Giroldi et al. [9] reasoned that neutron diffract may not be as sensitive as internal friction method to detect the dissolution of very fine (<100 atoms) precipitates in the very last stage of the hydride dissolution process. Consequently, they maintained that those fine precipitates will remain undissolved at the DSC peak temperature indicated by the coordinated DSC and ND measurements.

We believe that although IF technique may be more sensitive than ND (even though no evidence or reference has been presented in [9] to support this claim), similar to the interpretation of the DSC dissolution heat-flow signal, the interpretation of IF results is subjective and needs a more direct method to help interpret the signal. In contrast, the ND measurements provide a direct indication of the presence and volume fraction of hydride precipitates [8], which can help to validate the results of IF, DD and DSC techniques. Besides, the lack of sensitivity of ND to nano-scale structures at concentrations below 2 mg/kg H is within the typical uncertainty of H concentration measurements. Moreover, Pan and Puls [10] compare Young's modulus and IF results and do not report or discuss any DSC measurements. They show that in a pure Zr + 141 mg/kg H sample the maximum slope temperature on the IF signal corresponds to the knee point on the Young's modulus signal versus temperature and, therefore, conclude that the MST of IF signal is a point close to the end of hydride dissolution. Pan and Puls [10] also state that it is not possible to find the exact temperature above which all hydrides would be completely dissolved during heating. We also agree with this statement for experiments that employ none equilibrium conditions such as DSC and the techniques used in [10], which ramp the sample temperature at the rate of several °C per minute. In contrast, the ND measurements [8] have much longer waiting periods at each temperature and are believed to achieve near equilibrium conditions. Motivated by these discussions, we have carried out an equilibrium-type measurement (annealed the sample long enough to achieve definite equilibrium conditions) and compared the results to the DSC measurements to resolve the issue. In the present paper the results of these comparative measurements are reported. The present paper supports the neutron diffraction results [8] and shows that in DSC measurements, the peak temperature closely corresponds to the T_{TSSD} .

2. Experimental

A Zr–2.5Nb specimen, $1 \times 5 \times 30$ mm in size, was machined from a piece of unirradiated pressure tube aged at 400 °C for

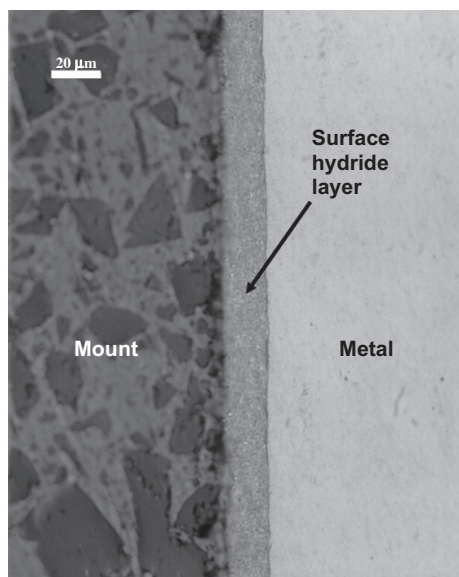


Fig. 3. Optical micrograph of the Zr-2.5Nb specimen electrolytically charged with hydrogen. The micrograph is showing almost no hydrides in the bulk of the specimen and a surface hydride layer of $\sim 17 \mu\text{m}$ thick.

100 h. The aged material was used to reduce the effects of any β -phase decomposition, during subsequent diffusion anneals (see below) and the DSC heating cycles, on TSS measurements [11]. The specimen was then electrolytically charged with hydrogen for 8 h in a 0.2 M H_2SO_4 acid bath at 60°C and a current density of 200 mA/cm^2 . Metallography showed that all sides of the specimen were covered with a solid hydride layer of $\sim 17 \mu\text{m}$ (Fig. 3). Three coupons of $1 \times 5 \times 5 \text{ mm}$ were cut from the specimen using a slow-speed Isomet saw.

The coupons were annealed to equilibrium (similar to Kearns' work [2]) in a TA Instruments DSC 2910³ equipment at nominally 250°C , 275°C and 300°C for 72, 35 and 24 h, respectively, using an isothermal process. During annealing, the actual temperature of the coupon was recorded (see Figs. 4a, 5a and 6a). Calculations, using a simple diffusion model, showed that less than one quarter of the actual annealing times were sufficient to bring the hydrogen dissolved within the bulk of the coupon to 99.99% of the solubility limit, the concentration in equilibrium with the remaining surface hydride layer. For example, 5 h annealing time was only needed at 300°C to achieve 99.99% of the solubility limit, but the coupon was actually annealed for 24 h to ensure that definitely the equilibrium conditions were attained. Simple mass balance calculations also showed that a $17 \mu\text{m}$ thick hydride layer on each side of the coupon is sufficiently thick that, at the end of the annealing-period, more than $13 \mu\text{m}$ would have remained. After annealing, the hydride layer was removed from all the surfaces of the coupons. To do this a layer of $\sim 50 \mu\text{m}$ was removed from each surface of the coupon using a 600-grit SiC paper. The process was carried out without any lubricant or coolant to avoid pick-up of any extra hydrogen by the coupon. The coupon was then analyzed to obtain the TSSD temperature using the same DSC equipment used for annealing the coupon. For DSC procedure and measurement details see [6,7]. Note that the annealing of the coupons to equilibrium with the surface hydride layers present and the subsequent DSC measurements after removing the hydride layers were carried out in the same DSC equipment, rather than in a different furnace, to avoid any additional temperature discrepancies.

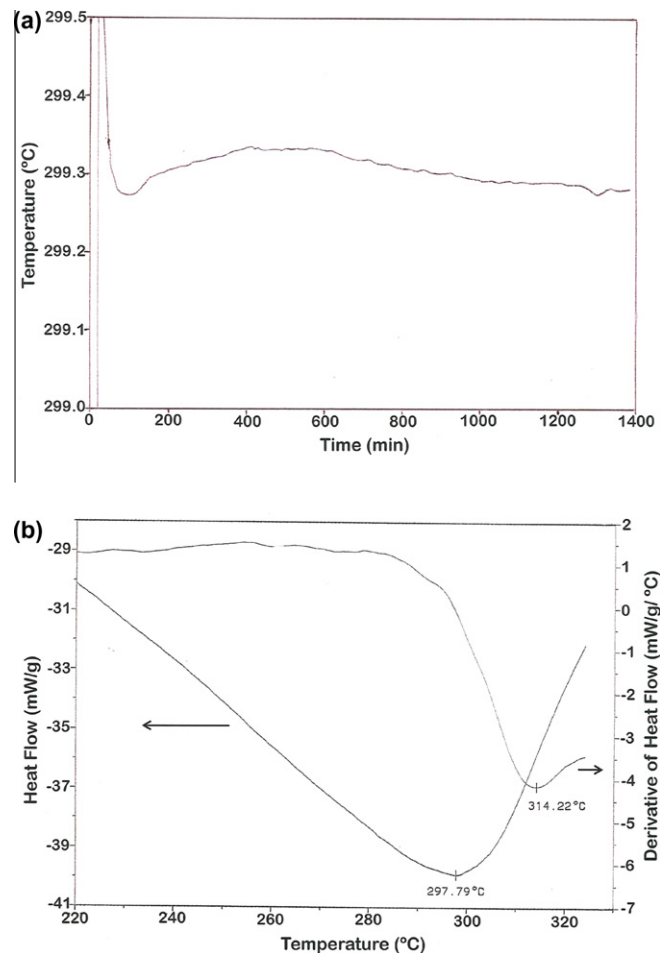


Fig. 4. Isothermal annealing record of coupon 1 with a surface hydride layer (a) and the result of a subsequent DSC run after removal of the surface hydride layer (b).

The DSC instrument was calibrated by a three-point method, using melting points of three standards: indium, tin and lead. For the present work, the reference was a hydrogen-free coupon of similar size and weight to the coupon under investigation. The hydrogen-free coupons have less than 1 mg/kg H and are produced by hot vacuum extraction method [12]. Each specimen was analyzed for the hydride dissolution temperature in several consecutive thermal cycles. The thermal cycles consisted of a heat up from ambient temperature, T_{min} , to some maximum temperature, T_{max} , followed by a cool-down to ambient temperature, with a hold-time of $\sim 5 \text{ min}$ at T_{min} and T_{max} .

3. Results and discussion

The first coupon was annealed to equilibrium in the DSC equipment at $299.3 \pm 0.1^\circ\text{C}$ for 24 h. For this process the DSC equipment was operated in an isothermal mode (Fig. 4a). Then, using procedures discussed above, the hydride layers were removed and the DSC measurements were carried out. In this case, the DSC run comprised of a total of seven consecutive cycles. In the first three cycles, the heating and the cooling rates were both 30°C/min . In the subsequent cycles the cooling rate was kept at 30°C/min , however, the heating rate was changed to 10°C/min for cycles 4 and 5 and 5°C/min for the last two cycles. The maximum temperature, T_{max} , achieved during the cycles was 340°C . The result of a typical DSC run is shown in Fig. 4b. The annealing temperature and time to equilibrium and the results of all the subsequent DSC runs for the first coupon are summarized in Table 1.

³ TA Instruments Inc., 109 Lukens Drive, New Castle, DE 19720-0311, USA.

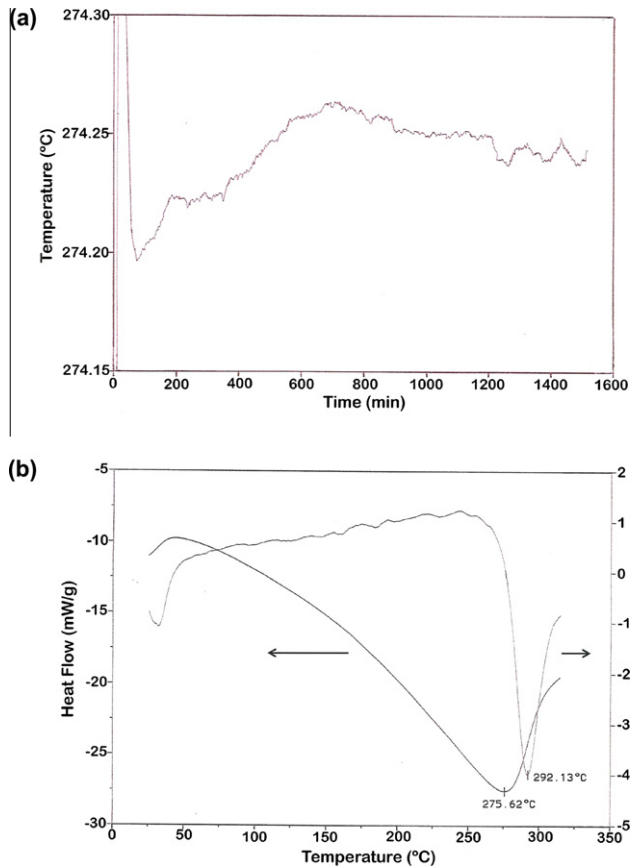


Fig. 5. Isothermal annealing record of coupon 2 with a surface hydride layer (a) and the result of a subsequent DSC run after removal of the surface hydride layer (b).

Table 1 shows that while the DSC PT is within 1 °C of the annealing temperature to equilibrium, 299.3 ± 0.1 °C, the MST, is ~ 15 °C higher. It also shows that at ~ 300 °C, both the PT and MST do not depend on the heating rate as long as the cooling rate is always kept at 30 °C/min. This shows that the 30 °C/min cooling rate causes the precipitation of fine hydrides. These hydrides seem to dissolve quickly during subsequent heating cycle.

The second coupon was annealed to equilibrium at 274.3 ± 0.1 °C for 35 h (Fig. 5a). Then the surface hydride layers were removed and the DSC measurements were carried out. For this coupon, compared to the first coupon, one additional cycle with heating and cooling rates of 30 °C/min was added to the end of DSC runs. The result of a typical DSC run is shown in Fig. 5b. The annealing temperature and time to equilibrium and the results of all the subsequent DSC runs for the second coupon are summarized in Table 2.

Table 2 shows that the PT is within about 1 °C of the annealing temperature, 274.3 ± 0.1 °C, and that the MST is ~ 16 °C higher. The table also shows that both the PT and the MST are slightly dependent on the heating rate (i.e., they are slightly closer to the annealing temperature at the lower heating rates than at the higher heating rates).

The third coupon was annealed to equilibrium at 249.3 ± 0.1 °C for 72 h (Fig. 6a). Then the hydride layers were removed and the DSC measurements were carried out. For this coupon also one additional cycle with heating and cooling rates of 30 °C/min was added to the end of DSC runs. The result of a typical DSC run is shown in Fig. 6b. The annealing temperature and time to equilibrium and the results of all the subsequent DSC runs for the third coupon are summarized in Table 3.

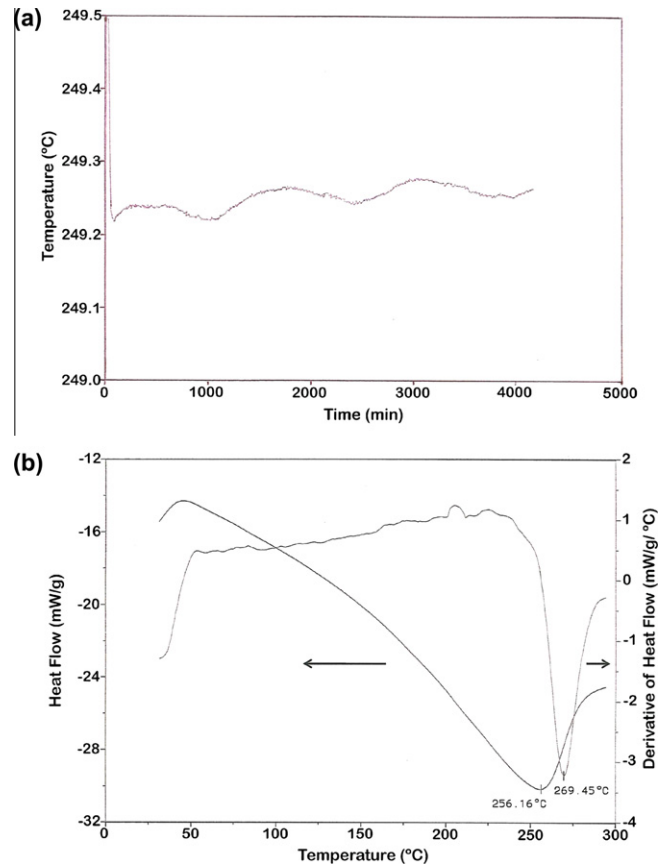


Fig. 6. Isothermal annealing record of coupon 3 with a surface hydride layer (a) and the result of a subsequent DSC run after removal of the surface hydride layer (b).

Table 1

Annealing temperature and time to equilibrium and the results of the subsequent DSC measurements for coupon 1.

Annealing temperature and time (see Fig. 4a)							
Temperature	Time						
299.3 ± 0.1 °C	24 h						
Ramp speed							
Heating	30 °C/min	10 °C/min	5 °C/min				
Cooling	30 °C/min	30 °C/min	30 °C/min				
DSC results with $T_{max} = 340$ °C							
DSC cycle	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
PT (°C)	300.7	297.8	298.7	298.8	298.7	298.6	298.7
MST(°C)	313.0	314.2	314.7	314.7	313.7	313.7	315.5

Table 3 shows that the DSC measurements carried out at about 249.3 ± 0.1 °C result in the PT being at least 3 °C higher than the annealing temperature. The MST is ~ 18 °C higher. At ~ 250 °C there also seems to be greater dependence on the heating rate for both PT and MST. This may be related to the fact that at lower temperatures the hydride dissolution rate is lower and, therefore, the higher heating rates may result in larger lag times and an overestimate of the dissolution temperature. However, it is somewhat puzzling that the trend is not reversed when the heating rate is returned to 30 °C/min (DSC cycle No. 8).

For comparison, all the results presented in Tables 1–3 are summarized in Fig. 7. In this figure the results of the DSC measurements from all three coupons are plotted against the coupon equilibrium annealing temperatures. A one to one line is added to the figure to make the comparison of the DSC data to the equi-

Table 2

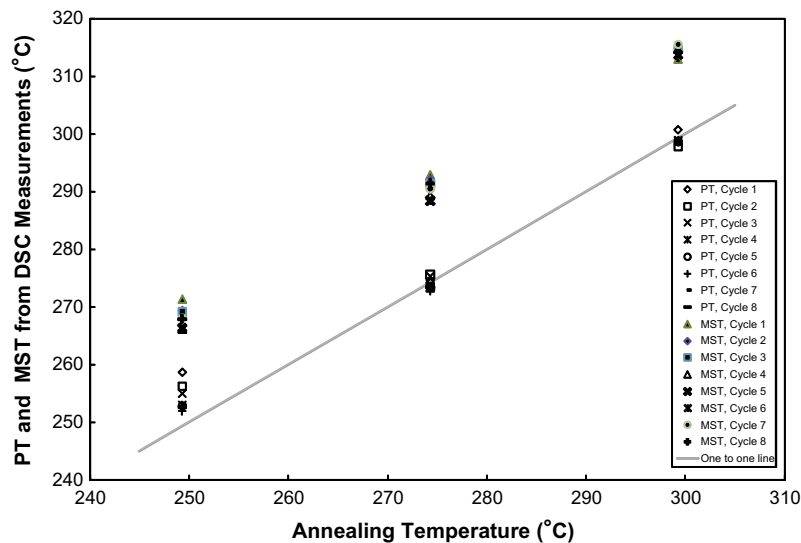
Annealing temperature and time to equilibrium and the results of the subsequent DSC measurements for coupon 2.

Annealing temperature and time (see Fig. 5a)								
Temperature			Time					
274.3 ± 0.1 °C			35 h					
Ramp speed								
Heating 30 °C/min			10 °C/min		5 °C/min		30 °C/min	
Cooling 30 °C/min			30 °C/min		30 °C/min		30 °C/min	
DSC results with $T_{max} = 320$ °C								
DSC cycle	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
PT (°C)	274.2	275.6	275.3	273.4	273.5	272.7	273.0	273.3
MST (°C)	292.9	292.1	291.4	289.3	288.4	288.4	290.5	291.4

Table 3

Annealing temperature and time to equilibrium and the results of the subsequent DSC measurements for coupon 3.

Annealing temperature and time (see Fig. 6a)								
Temperature			Time					
249.3 ± 0.1 °C			72 h					
Ramp speed								
Heating 30 °C/min			10 °C/min		5 °C/min		30 °C/min	
Cooling 30 °C/min			30 °C/min		30 °C/min		30 °C/min	
DSC results with $T_{max} = 300$ °C								
DSC cycle	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
PT (°C)	258.6	256.2	255.0	253.0	252.9	251.9	253.0	252.6
MST (°C)	271.3	269.4	269.1	266.1	266.4	266.2	268.0	267.9

**Fig. 7.** Results of DSC measurements versus coupon annealing temperatures. Note that the DSC PT results cluster much closer to the one to one line (i.e., the annealing temperature) than the DSC MST results.

librium annealing temperatures easier. Fig. 7 clearly shows that the DSC peak temperatures cluster much closer to the one to one line (i.e., the equilibrium annealing temperatures) than the DSC maximum slope temperatures. These results support the neutron diffraction results reported earlier [8] and show that in DSC measurements, the peak temperature closely corresponds to the hydride dissolution temperature T_{TSSD} .

As stated in the introduction, the techniques such as differential scanning calorimetry, which during the measurements ramp the sample temperature at the rate of several °C per minute, are not

suitable by themselves for studying the phenomena that require ample time to reach equilibrium. The only way that such measurements can be carried out with certain level of confidence is that the results at some point are compared with the results of some equilibrium-type measurements. Such process has been demonstrated in the present work, which shows that the DSC technique can be useful to study the dissolution of hydrides in the Zr alloys, if the heat-flow curve is interpreted properly by the aid of other equilibrium or near equilibrium type techniques such as the one employed here or neutron diffraction reported earlier [8].

4. Conclusions

A set of coordinated equilibrium-type annealing and DSC measurements were carried out to determine the part of the DSC heat-flow signal (i.e., “peak temperature”, “maximum slope temperature” or “completion temperature”) that closely correspond to the TSSD temperature. The results show that the TSSD temperature is much closer to the DSC peak temperature than the maximum slope temperature, confirming the earlier findings by a coordinated DSC and neutron diffraction measurements.

Acknowledgements

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