

## Dissolution and Precipitation Behavior of Hydrogen by Differential Scanning Calorimetry in Zr-2.5% Nb Pressure Tube Material

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### 1. Introduction

Zr-2.5%Nb alloy, which is excellent in high-temperature strength, corrosion resistance, and neutron absorption cross-sectional area, is used for pressure tube material in pressurized heavy water reactor (PHWR). Since the primary water flows through the pressure tube during the operation of PHWR, some of the hydrogen reacted with Zr is absorbed into the pressure tube [1]. The pressure tube materials containing hydrogen tend to precipitate hydrides ahead of notch or crack when the hydrogen concentration exceeds the solubility of hydrogen during cooling process of pressure tube. The precipitation of hydride lowers stress intensity factor for DHC initiation of the pressure tube materials. Furthermore, precipitation of hydride causes crack initiation and propagation by the delayed hydride cracking mechanism [1].

There are several studies on terminal solid solubility of dissolution (TSSD) and precipitation (TSSP) of hydrogen in Zr-Nb alloys using differential scanning calorimetry (DSC). Khatamian [2, 3] measured the TSSD of hydrogen in Zr-Nb alloys with different Nb concentrations and different levels of  $\beta$ -Zr decomposition. He found that the TSSD approaches the values of unalloyed Zr as the decomposition of  $\beta$  phase is increased and the Nb percentage of the alloy in  $\alpha$  Zr is decreased. The highest limit of solubility (7-9 times greater than  $\alpha$  Zr) was obtained for the annealed Zr 20 wt. % Nb alloy which is  $\beta$  Zr.

In this study, TSSD and TSSP in Zr-2.5% Nb pressure tube material are determined by maximum slope temperature (MST) during heating and cooling, respectively, using differential scanning calorimetry (DSC).

### 2. Experimental

The pressure tube material used in the experiment is Zr-2.5% Nb alloy. The chemical composition is shown in Table 1. The material of the pressure tube was cut into  $30 \times 100$  mm pieces. Hydrogen was charged in a 1-mol sulfuric acid solution at a current density of  $100\text{mA}/\text{cm}^2$ . The solution temperature is maintained to be  $85 \pm 5^\circ\text{C}$  for 24 to 40 hours. After hydrogen charging, the specimen was homogenized in vacuum sealed tubing for 240 hours at  $240\text{-}550^\circ\text{C}$ . The hydrogen concentration of the homogenized specimen was analyzed by using vacuum extraction method. The hydrogen concentration is determined by the average of three specimens. The hydrogen concentration varies from 12 to 144 ppm.

A DSC analysis was used to determine terminal solid solubility of dissolution (TSSD) during heating and

terminal solid solubility of precipitation (TSSP) by measuring DSC during heating and cooling, respectively.

Table 1. Chemical composition of Zr-2.5% Nb (wt. %).

Zr	Nb	Fe	O	N	P
97.4	2.5	0.05	0.097	0.007	0.003

Table 2. TSSD with hydrogen concentration in Zr-2.5% Nb pressure tube material.

Hydrogen Concentration (ppm)	Dissolution temperature ( $^\circ\text{C}$ )
12	194
28	240
86	324
33	269
54	305
81	318
82	324
144	378

### 3. Results and Discussions

The specific heat variation with heating and cooling of 28-ppm specimen is shown in Fig. 1. The specific heat increases with temperature up to  $230^\circ\text{C}$  and decreases at above  $230^\circ\text{C}$ . The MST is defined by derivative of DSC (DDSC) curve. The MST in 28-ppm specimen is  $240^\circ\text{C}$ . This is TSSD for 28-ppm specimen. The TSSP can be determined by a similar method during cooling.

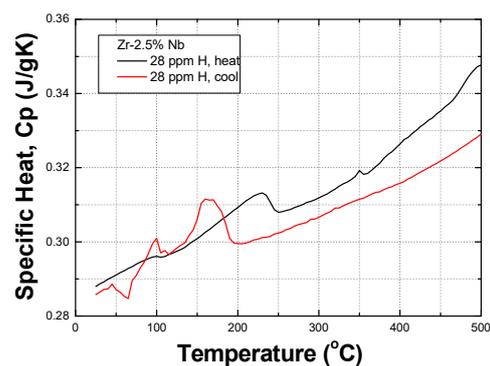


Fig. 1. Specific heat variation during heating (black line) and cooling (red line) in Zr-2.5% Nb pressure tube material with 28ppm.

The specific heat variation with heating and cooling of 86-ppm specimen is shown in Fig. 2. The specific heat increases with temperature up to  $310^\circ\text{C}$  and decreases at above  $310^\circ\text{C}$ . The MST is defined by derivative of DSC

(DDSC) curve. The MST in 86-ppm specimen is 324 °C. This is TSSD for 86-ppm specimen. The DSC and DDSC curves in 28 and 86-ppm specimen are shown in Fig. 3.

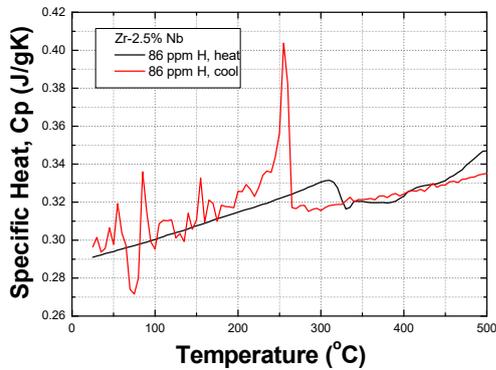


Fig. 2. Specific heat variation during heating (black line) and cooling (red line) in Zr-2.5% Nb pressure tube material with 86ppm.

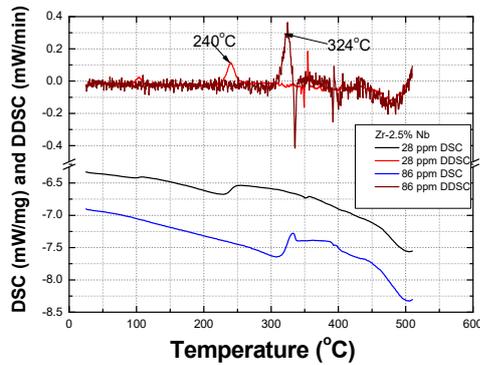


Fig. 3. Results of DSC and DDSC (derivative of DSC) curves in Zr-2.5% Nb pressure tube material with 28 ppm (black line) and 86 ppm (blue line).

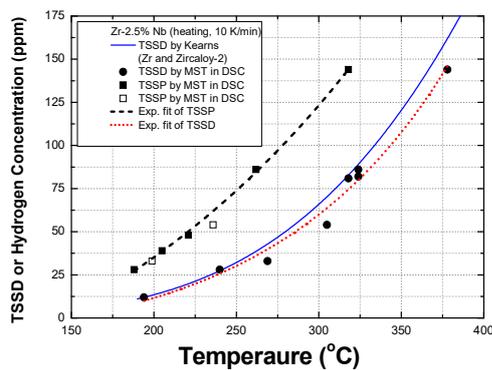


Fig. 4. TSSP and TSSD curves determined by DSC in Zr-2.5% Nb pressure tube material compared with Zr and Zircaloy-2 by Kearns [4].

The relationship between TSSD and hydrogen concentration is shown in Fig. 4. The TSSD is very similar to TSSD by Kearns [4] as shown in red dotted

line, even though the Zr-2.5% Nb alloy is consisted of  $\alpha$  and  $\beta$  phases whereas the materials used by Kearns are single  $\alpha$  phase. The TSSP is lower than TSSD by about 60 °C. These results are consistent with a recent investigation by Parodi et al. [5]. This seems because the major phase of various Zr alloys is  $\alpha$ -Zr.

#### 4. Conclusions

1. The MST by DSC is a useful method to determine TSSD and TSSP in Zr-2.5% Nb pressure tube material.
2. The TSSD with hydrogen concentration is very similar to work done by Kearns through a diffusion experiment in  $\alpha$ -Zr alloys.
3. There is little difference in TSSD in various commercial Zr alloys.
4. The precipitation of hydride requires undercooling by about 60°C from TSSD.

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