

## Study of Dissolution and Precipitation Reaction of Hydride in Zr-2.5%Nb Pressure Tube Material using DSC (differential scanning calorimeter)

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### 1. Introduction

The pressure tube is the primary pressure boundary containing the fuel of the CANDU (CANadian Deuterium Uranium) reactor. The pressure tube made of Zr-2.5% Nb alloy is damaged by delayed hydride cracking (DHC) mechanism by absorbing deuterium generated by reaction with coolant during. Until now, this damage mechanism is the most important one that impedes the operational stability of the heavy water reactor [1].

The precipitation of hydrides by the penetration of hydrogen in the pressure tube material is due to the fact that the amount of hydrogen precipitated in the hydride exceeds the amount that can be employed in the material so far. However, it is known that the DHC phenomenon due to the precipitation of hydrides occurs even within the solubility limit of hydrides around defects. Therefore, it is very important whether hydrogen lag breakdown can occur in the heavy water operation environment, and therefore the hydrogen concentration during operation in the pressure pipe should be tracked in an appropriate manner.

The hydrogen lag breakdown phenomenon in the pressure tube material is due to the precipitation of the hydride, but the reaction to decomposition or precipitation of the hydride has not been systematically studied. In this study, we investigated these reactions by measuring the activation energy for decomposition and precipitation of hydrides by heating the specimens loaded with hydrogen at different heating rates using DSC.

### 2. Experiments

Hydrogen was charged by electrolytic method to Zr-2.5% Nb pressure tube material at  $85 \pm 5^\circ\text{C}$  at a current density of about  $100 \text{ mA/cm}^2$  for 24 hours. To prevent oxidation during the homogenization treatment, Pyrex tubing was applied and the tubing was homogenized at  $350^\circ\text{C}$  for 24 days. The amount of hydrogen was analyzed by using the specimen from which the hydride formed on the surface was removed. The specimens were subjected to DSC (differential scanning calorimeter) analysis during heating and cooling. During heating and cooling, the peak temperature for the endothermic and exothermic reactions was measured in order to determine the

activation energy for the endothermic and exothermic reactions.

### 3. Results and Discussions

The results of the DSC analysis of the pressure tube material containing 86 ppm are shown in Fig. 1. The DSC curve goes downwards when an exothermic reaction occurs, and downwards when an endothermic reaction occurs. The characteristic of DSC analysis is basically that as the heating rate is increased, the time for holding the material at a specific temperature is shortened, so that the temperature of the endothermic reaction or exothermic reaction is also increased.

Using this principle, the activation energy for a specific reaction can be obtained by Kissinger plot [2]. Therefore, DSC analysis is very useful to investigate the phase transformation of material. When a specimen containing 86 ppm of hydrogen is heated at  $40 \text{ K/min}$  in this experiment, an endothermic peak appears at  $316.2^\circ\text{C}$ .

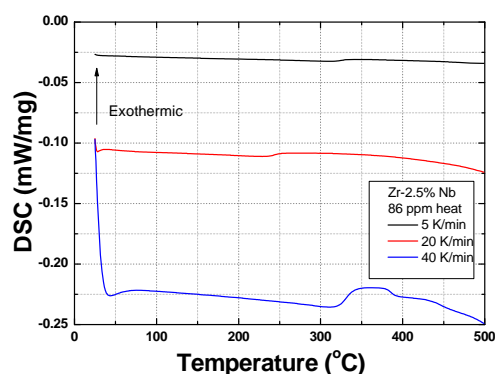


Fig. 1. DSC curves with heating rate in Zr-2.5%Nb pressure tube material with 86ppm Hydrogen.

Zr-2.5% Nb alloy charged with 86 ppm hydrogen shows an endothermic reaction when hydrides decompose during heating. Table 1 summarizes the peaks of endothermic reaction when heating specimens containing 86 ppm hydrogen at 10, 20, and  $40 \text{ K/min}$ . In the cooling process, exothermic reactions are observed. The results of the measurements with varying cooling rates are summarized in Table 2. Based on these results, the activation energy for the endothermic and exothermic reactions was found to be  $-431 \text{ kJ/mole}$  for the endothermic reaction and  $+256 \text{ kJ/mole}$

for the exothermic reaction. The activation energy for the endothermic reaction is plotted in Fig. 2.

The sign of the activation energy in the heating and cooling process depends on whether it is an endothermic reaction or an exothermic reaction. The activation energy of 431 kJ / mole in the process of decomposition of hydride during heating is at least 110 kJ / mole higher than the activation energy of 150-320 kJ / mole for self-diffusion of Zr [3, 4]. This seems to be due to the fact that the decomposition process of the hydride is not controlled only by the diffusion of Zr, but involves the certain process.

Table 1. Peak temperature variation with heating rate in Zr-2.5%Nb pressure tube material with 86 ppm hydrogen during heating.

heating [K/min]	peak [C]	1/T (K <sup>-1</sup> )	alpha/T2
10	307.9	0.00172102	2.96192E-05
20	310	0.00171482	5.88125E-05
40	316.2	0.00169678	0.000115163

Table 2. Peak temperature variation with cooling rate in Zr-2.5%Nb pressure tube material with 86 ppm hydrogen during cooling.

cooling [K/min]	peak [C]	1/T (K <sup>-1</sup> )	alpha/T2
5	260	0.0018756	1.75902E-05
10	257.5	0.0018844	3.55127E-05
20	248	0.0019188	7.36384E-05
40	242.7	0.0019385	0.000150319

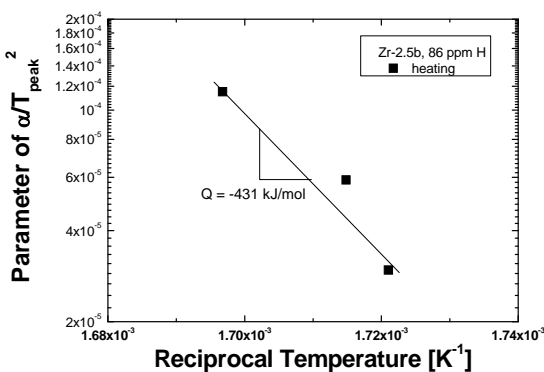


Fig. 2. Activation energy for hydride dissolution during heating by DSC in Zr-2.5%Nb pressure tube material with 86ppm Hydrogen.

It is known that the equilibrium hydrogen concentration at 350°C was 120 ppm, but the hydrogen concentration analysis showed 86 ppm. A method of charging hydrogen into a Zr-2.5% Nb alloy is to form a hydride on the surface and allow hydrogen to diffuse

into the material through homogenization. The material with hydride on the surface was vacuum sealed to Pyrex and put into an electric furnace maintained at 350°C. However, the temperature of Zr-2.5% Nb alloy in Pyrex tubing did not reach 350°C and reached about 320°C, since the equilibrium hydrogen concentration at 325°C is 90 ppm.

#### 4. Conclusions

The activation energy for decomposition of hydrides in the heating process of Zr-2.5% Nb pressure tube material containing 86 ppm of hydrogen was 431 KJ / mole. This suggests that the decomposition process of the hydrides is not determined solely by the diffusion of Zr. At present, the decomposition process of hydrides is not fully understood, but at least other processes other than the diffusion of Zr occur simultaneously. The activation energy for the precipitation of hydrides in the cooling process after DSC analysis was 256 kJ / mole. This value is similar to the activation energy value for Zr self-diffusion.

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